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CONTENTS

General Subjects PAGE

Rubber Division Activities..... xvii

New Books and Other Publications..... xx

Reprinted Papers

The Carbon Reinforcement of Rubber. By W. B. WIEGAND..... 395

Change of Volume of Rubber on Stretching: Effects of Time, Elongation, and Temperature. By WILLIAM L. HOLT and ARCHIBALD T. MCPHERSON.... 412

Isoprene and Rubber. Part 46. Viscosity Measurements of Gel Solutions of Rubber and Hydrorubber. By H. STAUDINGER and H. P. MOJEN.... 432

Isoprene and Rubber. Part 47. The Decomposition of Rubber by Acids. By H. P. MOJEN..... 445

Some Physical Properties of Isoprene. By NORMAN BEKKEDAHL, LAWRENCE A. WOOD, and MIECZYSLAW WOJCIECHOWSKI..... 451

Note on the Diffraction of X-Rays by Old Specimens of "Frozen" Rubber. By WILLIAM H. BARNES..... 462

The Constitution of Inorganic Rubber. By ARMAND MARIE DE FICQUELMONT.....465

Chlorination of Polymers of Chloroprene Rubber. By A. KLEBANSKIĬ and M. RAKHLINA..... 467

The Vulcanization of Rubber by Diazoamino Compounds. By T. G. LEVI 471

Purified Rubber for Electrical Insulation. By A. R. KEMP..... 474

The Use of Acetylene in the Rubber Industry. By PAUL WALTER..... 492

Entered as second-class matter May 12, 1928, at the Post-Office at Easton, Pennsylvania, under the act of August 24, 1912.

Tests on Crepe Soling. III. Water Absorption. By T. H. Messenger and J. R. Scott 500
Mastication and Rate of Set-Up. Part I. By S. Buchan 508
Secondary Changes during Vulcanization of Ebonite. Part I. By B. L. Davies 516
Properties of Hard Rubber. III. Study of Surface Resistivity as Affected by Exposure to Light, Air, and Humidity. By H. F. Church and H. A. Daynes 532
Studies on Vibration Tests of Rubber. By Shohei Saito and Katsumi Ishiguro 556
Rubber-Lined Equipment. Fundamental Principles of Design. By J. R. Hoover and H. C. Klein 564
Contributions to the Analysis of Rubber. I. Determination of the Water-Soluble Components of Rubber. By P. Dekker 574
Physical Testing of Latex Films. By C. F. Flint and W. J. S. Naunton ... 584
Examination of Rubber Latex and Rubber Latex Compounds. I. Physical Testing Methods. By H. F. Jordan, P. D. Brass, and C. P. Roe 615
Determination of Free Carbon in Rubber Goods. By E. W. Oldham and J. G. Harrison, Jr. 635
The Preparation of Thin Films. By T. P. Sager 639

RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

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To these charges of $2.00, $4.00, and $6.00, respectively, per year, extra postage must be added at the rate of $.20 per year for subscribers in Canada, and $.50 per year for those in all other countries not United States possessions.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, C. W. Christensen, Monsanto Chemical Company, 1012 Second National Building, Akron, Ohio.

Articles, including translations and their illustrations, may be reprinted if due credit is given Rubber Chemistry and Technology.

Rubber Division Activities

The Rubber Division of the American Chemical Society

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The Rubber Institute of France

The Rubber Institute of France was initiated by the Union of Planters and the Rubber Planters' Association of Indo-China, and was organized towards the end of 1936 by a group of experts, with a view to extending the applications of rubber through extensive scientific research. The activities which are planned are based on what experience indicates to be desirable.

First of all there is to be international coöperation, which is, more than ever before, the most effective way of stimulating discovery and progress. The Rubber Institute of France will not therefore let any opportunity pass to enter into close relations with technical societies of other countries, to lend its assistance, and to cooperate in every undertaking of general utility.

In the second place, the literature and keeping of records will have all the care which their evergrowing importance deserves. A special library has already been started, and it will be enlarged as funds and opportunity permit. An effort will be made to encourage an interest in this field on the part of those who should profit most by these facilities, but who in many cases would not do so because of not being aware of their availability.

As soon as the necessary details of organization have been completed and the Institute has been established on a working basis, original investigations will, as might be expected, comprise the greater part of the activities. The general nature of the researches which are planned has been governed by certain problems already under investigation; but the researches will also be concerned with more immediate problems, with a view to coöperating in a practical way with investigators in other countries who are working towards the solution of problems of great practical importance to the rubber industry.

One of the most promising functions of the new Institute will be to coördinate the four groups responsible for the prosperity of the rubber industry, *viz.*, planters, manufacturers, consumers, and research workers. Although this attempt at coordination is concerned primarily with French interests, it is nevertheless perfectly possible that its influence will be felt elsewhere, just as helpful suggestions from abroad will be heartily welcomed.

It is also planned to organize a special coöperative service of the French Rubber Institute, the function of which will be to collaborate with similar organizations in

other countries, with a view to utilizing every opportunity to encourage and promote the use of rubber.

The resources at the disposal of the Rubber Institute now consist of funds originating in the French tax on exports of rubber from Indo-China, in accordance with the terms of the International Rubber Regulation Agreement.

In addition to this, an appeal is made to the generosity of both official and private sources in support and furtherance of this work of general concern and welfare.

The Rubber Institute of France is governed by an Executive Committee composed of the following members:

Ph. Langlois, President of the Rubber Institute of France, alternate representative of the Government of Indo-China on the Rubber Regulation Committee (F. Bernard, titular delegate).

H. Gourdon, Director of the Department of Economics of Indo-China, representing the Governor-General of Indo-China.

Ch. Dufraisse, Professor at the School of Industrial Physics and Chemistry.

M. Bos, Secretary-General of the French members of the Rubber Regulation Committee.

P. Petithuguenin, representing the Union of Rubber Planters in Indo-China.

P. Blanchard, representing the Commission of Rubber Planters of Indo-China.

The policies and supervision of the scientific work are vested in an Advisory Committee, composed of the following members:

M. Delépine, President, Member of the Institute, Professor at the Collège de France.

L. Blaringhem, Member of the Institute, Professor on the Faculty of Sciences of the University of Paris.

J. Duclaux, Professor at the Collège de France.

Ch. Dufraisse, Professor at the School of Industrial Physics and Chemistry.

P. Mensier, Engineer of Arts and Manufacture, representing the Rubber Commission.

Ph. Langlois, President of the Rubber Institute of France.

The Rubber Institute has appointed to the International Bureau of Rubber Research, formed in connection with the International Rubber Regulation Committee:

Ph. Langlois, President of the Rubber Institute.

L. Blaringhem, Member of the Advisory Committee.

The Rubber Institute has also appointed to the International Coöperative Committee, P. Petithuguenin, Member of the Executive Committee.

At least while it is being established, the Rubber Institute of France will have its offices in the Department of Organic Chemistry of the Collège de France, where Professor Delépine has very kindly offered to the Institute the freedom and use of the facilities of his laboratory, recently reconstructed and equipped in the most modern fashion. It is of interest that the famous chemist Marcellin Berthelot carried on his work in this same department where the new Institute was formed and that its President, Ph. Langlois, is a grandson of the renowned scientist.

A New Rubber Journal

Gomma

The first journal devoted to the chemistry and technology of rubber to appear in Italy commenced publication in January of this year. It is entitled *Gomma*, and is under the direction and editorship of the well known physicist and engineer, Dr. R. Ariano of Milan.

The first issue contains two contributions of new work, "The Vulcanization of Rubber by Diazoamino Compounds" by T. G. Levi of the Pirelli Company and "The Brittleness of Ebonite" by R. Ariano. It also contains a review and discussion of "Pneumatic Tires and Agricultural Machines" by Ariano, and six abridged translations into Italian of articles on rubber chemistry and technology which have appeared in various journals. If this first issue is indicative of what is to be expected in future issues, rubber chemists and technologists may be confident of the appearance of many interesting and valuable contributions to rubber chemistry and technology. Our Italian colleagues in the rubber industry and in the universities who are adding to our knowledge of the chemistry and technology of rubber are to be congratulated for the inauguration and support of a journal in their own language. It is hoped to make available in English some of the contributions which appear in the new journal *Gomma*, in fact the first of these is to be found on page 471 of this issue of RUBBER CHEMISTRY AND TECHNOLOGY.

New Books and Other Publications

Gomma. A bimonthly journal. Volume 1, No. 1, is dated January–February, 1937. Director and Editor, Dr. A. Ariano. Administration and Editorial Offices, Via Spontini N. 5, Milano, Italy. Subscription, 40 lire per year outside of Italy; single issue 5 lire. This new rubber journal, devoted to rubber chemistry, physics, technology, engineering, statistics, etc., is described more fully on page xix of this issue of RUBBER CHEMISTRY AND TECHNOLOGY.

Gum-Elastic and Its Varieties, with a Detailed Account of Its Applications and Uses, and of the Discovery of Vulcanization. By Charles Goodyear. New Haven, **1855**. Vol. I, 246 pp.; Vol. II, 379 pp., but the pagination is somwhat irregular. Reproduced for the *India-Rubber Journal* on the Birmingham Public Libraries' Photostat. London: Maclaren and Sons, Ltd., **1937**. Two volumes in one. Price, 15s. 0d.

To those of us who have the time and inclination to study the beginnings of things, the appearance of this classic in an accessible form is an event of importance. The foundations of the whole rubber manufacturing industry were laid about the same time by Thomas Hancock in England and by Charles Goodyear in the United States, and the influence of these two pioneers persists to the present day. Hancock's work is comparatively well known among rubber men through the publication of his "Personal Narrative," but details of Goodyear's romantic career have been largely veiled in mystery and tradition.

This is through no fault of Goodyear himself, who put his work on record in great detail, but rather to the rarity of copies of his book. The initiative of Mr. Gale, editor of the *India-Rubber J.*, has put an end to this once and for all. The present issue is no mere reprint. It is a photographic copy of the 1855 original in the Birmingham Public Library, and contains all the errors and omissions of that original, so eloquent of the author's harassed life. The value of this copy is greatly enhanced by several pages of introductory matter reciting concisely the history of Goodyear's discoveries.

Volume I gives a detailed account of caoutchouc as it was known in the 1850's, together with an account of Goodyear's own tireless experiments, disappointments, difficulties, and final triumph. Like many another after him, he found that the way of inventors is hard, and he devotes two chapters to a discussion of the unhappy position of the impecunious patentee and of how the patent laws in his day seemed framed especially for the encouragement of pirates! Volume II is devoted to a detailed review of the applications of vulcanized rubber.

The publishers are to be congratulated on making this valuable work generally available, and we predict for it a wide success. The reviewer does, however, harbor some small disappointment at the binding and paper, which he had hoped would be more in keeping with the solid worth and antiquity of the subject matter, and would resemble the substantial but sober appearance of the works of a past generation. [*Journal of Rubber Research.*]

The Rubber Book. By William Clayton and Helen Sloman Pryor. Published by Harcourt, Brace and Co., 383 Madison Avenue, New York City. 100 pp. 6 × 9 in. $1.00.

This book is one of a series of story-picture books on important industries written and prepared by Mr. and Mrs. Pryor. The purpose of these books is to present

specific information to gratify children's curiosity without confusing them by too many details. The Rubber Book is evenly divided with text and photographs, many of the photographs being originals. Each text page is devoted to some other phase of rubber—from cultivation to use—while the pictorial illustration on the opposite page bears out the text. Although told in story-book fashion, and intended for children, the accurate tracing of rubber from plantation to use, plus the attractiveness and distinction of most of the photographs, recommends this volume to adult attention. [*The Rubber Age* of New York.]

Compounding Materials Used in the Rubber Industry (Classification and Health Hazards). National Safety Council, 20 North Wacker Drive, Chicago, Ill. 16 pp. $8\frac{1}{2} \times 11$ in.

Including material from papers presented at various meetings of the Rubber Section of the National Safety Council, this pamphlet has been revised and brought up to date by L. J. D. Healy, technical superintendent, Fisk Rubber Company, Cudahy, Wisconsin. It is a compilation of experience in accident prevention, and should not be confused with Federal, State, or insurance requirements or with national safety codes. Accelerators, antioxidants, and dry organic compounds are classified by chemical groups, and the origin, constitution, uses, and health hazards of each group are given. The pamphlet is recommended to every rubber executive entrusted with plant safety. [*The Rubber Age* of New York.]

Centennial Celebration of the American Patent System. 1836–1936. A report written by the National Committee of the Centennial Celebration. Paper, $11 \times 8\frac{1}{2} \times \frac{3}{8}$ in. Printed by United States Government Printing Office, Washington, D. C.

This book of 85 pages describes in complete detail the celebration of the one hundredth anniversary of the American Patent Office. The speeches given by the various prominent men traced the development of inventions from the earliest times to the present. The development of the American patent system and its influence on the economic well being of the general public was presented by Thomas Ewing, a former commissioner of patents. Dean Kimball spoke on the influence of the great inventions of the past century on making our modern life the complex structure it is. Another speaker dealt with the tendency of future inventions to be the product of organized group study by professional inventors, as opposed to the individual inventors of the past, and the possible threats to future invention brought about by over-zealous government interference. "Research on Parade" showed some of the recent outstanding achievements in science and their probable influence on the future economic and social standards. Considerable space is given to the banquet—a "Patented" Dinner, where the menu was printed with patent numbers instead of the names of the foods. By viewing the menu through a special synthetic glass the names of the foods represented by the patents were visible. During the dinner "Voice of Progress" talked about the 12 most eminent inventors, of which Charles Goodyear was one. [*India Rubber World.*]

Glossary of Terms for Rubber Manufacturers. Stamford Rubber Supply Company, Stamford, Conn. $4\frac{1}{2} \times 7$ in.

This is the second edition of the glossary of rubber terms, the first of which was issued by the company in 1935. The new edition contains many terms and definitions not previously included, while many of the original definitions have been sim-

plified and clarified. The booklet also embodies the advantages to be gained by the use of factice in rubber manufacturing processes. [*The Rubber Age* of New York.]

Evaluating Carbon Black for the Rubber Industry in the Huber Laboratory. J. M. Huber, Inc., 460 West 34th St., New York, N. Y. Cloth, 8 by $10^1/_4$ in. 44 pp. 22 illus.

This concisely written book on carbon black for the rubber industry is in four parts. The first, dealing with rubber laboratory standard procedure, covers the preparation of rubber stocks from compounding to cooling the cured stocks. Part II treats of physical tests, including stress-strain tests, aging of rubber stock, abrasion, T-50, flexometer, tear resistance, rebound, plasticity and dispersion tests, and determination of specific gravity and hardness. Analytical tests, in Part III, deals with volatile matter, accelerator adsorption, acetone extraction, grit, moisture, ash. Part IV is a story in pictures showing the production of carbon black.

As the foreword so aptly expresses it: "This book, illustrating the apparatus and describing the several tests, is not intended to present a discussion as to the significance of results, nor the striking correlation of the various tests; but, rather, it is intended to promote a standardization of tests, their objectives and procedure, and to be generally helpful to those discriminating users of carbon black who will be interested in exploring with us the lesser known—though perhaps vitally important—characteristics of the pigment."

This review would not be complete without some word of praise regarding the excellent typography and superb pictures used in this book. Huber is to be congratulated upon the fine job done. [*India Rubber World.*]

Proceedings of the Thirty-Ninth Annual Meeting of the A.S.T.M. Held at Atlantic City, N. J., June 29 to July 3, 1936. Vol. 36. American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa. Illustrated with subject and author indices. Each part costs: $5.50 in stiff paper cover; $6 cloth; and $7 half leather.

Part I (1245 pages) contains the reports of 45 standing committees, and includes 115 tentative specifications and test methods. There are extensive reports on ferrous and non-ferrous metals as well as ceramic and concrete materials. Some of the reports deal with rubber products for friction tapes and insulated wire. Other reports cover accelerated aging, adhesives, tension testing, and compression set of vulcanized rubber.

Part II (846 pages) contains the eleventh Edgar Marburg lecture by Arthur L. Day on "Developing American Glass" and 50 technical papers, with extensive discussions following each paper. There are five papers given in the "Symposium on the Limitation of Laboratory and Service Tests in Evaluating Rubber Products." These papers deal with tires, footwear, automotive rubber parts, belts, hose, and insulated wire and cables. Several papers on the subject of boiler feed water are included. There is also an extensive treatise on methods of determining gloss in connection with various types of materials, and an article on the testing of organic finishes. [*India Rubber World.*]

Compounding Materials Used in the Rubber Industry. Industrial Safety Series No. Ru. 1, Part I—Accelerators, Antioxidants, and Dry Organic Compounds (Classification and Health Hazards). National Safety Council, 20 North Wacker Drive, Chicago, Ill.

This 16-page pamphlet, a compilation of experience in accident prevention, is the first of a series of pamphlets being published on the subject groups:

(1) Accelerators, Antioxidants, and Dry Organic Compounds; (2) Dry Inorganic Compounds; (3) Gums, Resinous Materials, and Waxes; (4) Liquids and Bases. In addition to the listing in four groups according to their toxicity, this pamphlet presents an alphabetical classification in which the compound or chemical is described as to: (1) origin, identification, and chemical characteristics; (2) general use in the industry; (3) health hazards and any suggestions, if necessary, to reduce or eliminate such hazards. This pamphlet is a revision of an original pamphlet prepared from a paper given by L. J. D. Healy, then technical superintendent of The Fisk Rubber Co., Cudahy, Wis., before the Rubber Section during the Sixteenth Annual Safety Congress (1927). In December, 1929, *India Rubber World* published the listing according to toxicity, covering the greater portion of the materials included in this pamphlet. [*India Rubber World.*]

Directory of Association Members. Association of Consulting Chemists & Chemical Engineers, Inc., 50 E. 41st St., New York, N. Y.

The main part of this 60-page directory is devoted to describing each firm of consultants: organization; personnel, and scope of activities. There are also several indices: (1) an alphabetical list of members as of November 1, 1936, including the names and addresses of the firms with which they are associated; (2) a numerical list of the members' certificate numbers; (3) a geographical list of the members according to states; (4) a functional list showing the fields in which the members are qualified. There are two firms listed as being specially qualified in the rubber field, and five who are generally qualified. [*India Rubber World.*]

[Reprinted from Canadian Chemistry and Metallurgy, Vol. 21, No. 2, February, 1937.]

The Carbon Reinforcement of Rubber

W. B. Wiegand

COLUMBIAN CARBON CO., 41 EAST 42ND ST., NEW YORK CITY

Part I—Its Course

Evolution

Discovered in England in 1910 where, however, insufficient quantities were used, and developed commercially in Akron in 1912, its evolution may be roughly divided into three periods: 1913–1920, during which time the art led the science; 1920–1927, during which time science led the art, and 1927–1934, when the art once more overtook the science, leading to the empirical employment of 50 per cent or more of carbon on the rubber. At the present time there is needed a fresh theoretical approach.

The Course

The scope of carbon reinforcement may conveniently be defined as the region of positive Delta A values. The shape of the Delta A curve is in itself interesting as to symmetry, the presence of a well-defined maximum, and the extraordinary extent of positive values compared to other reinforcing pigments.

Position of Maximum

The published data on carbon Delta A functions have been assembled together with fresh data, the latter including both litharge and Captax accelerated mixings. Considerable discrepancies appear. A mean curve has been drawn to include the recent data, and previous work in which fatty acids were employed. This mean Delta A curve for carbon black shows a maximum at 26.3 per cent by volume of carbon on the rubber, corresponding to 51 per cent by weight. This mean curve cuts the base-mixing energy axis at 53.6 volumes of carbon, or approximately 105 per cent by weight.

Analysis of Delta A Curve

(See Figure 1)

Region A, from 0 to approximately 12.5 volumes (24 per cent by weight), is characterized by the following properties: energy absorption rising rapidly and linearly, rebound resilience high and decreasing only slowly, electrical resistivity and breakdown voltage begin sharp decline, hysteresis low. Mixings in this region of carbon reinforcement are suitable for solid tires, electrical insulation next to the wire (for moderate voltage), shoe uppers, etc. General properties of carbon stocks in this region are toughness plus liveliness.

Region B extends from Region A to the point of maximum wear-resistance, taken as lying between 30 and 35 volumes. The line of demarcation is less sharply developed than that between A and B. Region B is characterized by the following properties: maximum resistance to "wear and tear," maximum energy absorption (26.3 volumes = 51 per cent by weight), and point of inflection of rebound resilience-

loading curve (27.1 volumes = 52.5 per cent). At this point energy absorption equals 228 per cent of base mixing.

Throughout Region B, rebound resilience declines rapidly and for the most part linearly. Modulus increases throughout this region, and may with profit be looked upon as a measure of energy absorption values at the lower elongations (prior to rupture). The mechanism of "impact" abrasion as in the case of tire treads is complex, but undoubtedly is influenced not only by energy absorption to rupture but also by energy absorption before rupture. The fact that the latter value continues to increase, after the former has reached its optimum and is already declining, probably explains why the point of maximum wear-resistance lies well to the right of the energy absorption or proof resilience optimum.

The exact position of this wear-resistance optimum loading depends on conditions, speed, road surface, etc., but has been stated to lie between 30 and 35 volumes. At this point also the rebound resilience curve reverses its curvature, becoming convex to the loading axis. Also at this point the energy absorption curve begins to decline rapidly. For this reason the upper boundary of Region B has been tentatively fixed at approximately 33 volumes. Further study may require placing it still farther towards the right.

Region B has at the present time the highest economical importance, being represented by tire treads, conveyor belt covers, insulated wire jackets, rubber footwear solings, etc. The exact proportion of carbon will be influenced by the nature of service, processing requirements, design of carcass, non-skid pattern, tread thickness, etc. Present practice for tire treads is to load with 50 to 55 per cent, after allowance of several per cent for flying losses.

Region C extends from Region B up to the limits of reinforcement and beyond. The upper limit under existing conditions is fixed by elongation at rupture as a factor in flex-resistance of high carbon tap soles. Region C represents an unique combination of properties unapproached by any other pigment than carbon, making possible rubber articles exhibiting in combination high modulus and stiffness, good tensile, good elongation plus leather-like, plastic consistency.

Its chief application at the present time is in high carbon molded rubber solings,* and also in mechanical rubber goods specialties, such as motor couplings. The compounding of carbon in Region C necessitates close attention to fatty acid content, proper mixing and refining, special precautions when reclaimed rubber is present (separate master batches), special precautions in estimating proper technical cure, and selection of proper grade of carbon.

How Best to Reinforce

(With Special Reference to Region B)

Dispersion.—The problem in the case of a tire tread is to spread two pounds of rubber over ten acres of carbon. The attainment of perfect dispersion is much more difficult to recognize than in the case of the paint and lacquer industries, where color, tone, and gloss provide sensitive ocular criteria. Microscopic evaluation of degree of dispersion in rubber is difficult and may even be misleading because, while affording some evidence of the existence of undispersed agglomerates, it affords no clue to the nature and condition of the properly dispersed material. A low-grade, coarse-particle carbon may thus show an emptier microscopic field than finer, harsher, but far better wearing carbon.

Electrical properties provide a sensitive clue to the state of dispersion of carbon

* See U. S. Patents 1,465,504, 1,578,875; Canadian Patents 229,369, 274,299, 248,087, 250,918.

in rubber. Thus proper masterbatching has shown enormous improvements in resistivity, double values for electrical breakdown, lower dielectric constants, and lower power factors. The stress-strain curves for tire treads prepared with and without master grinds show in the case of the former higher tensile, higher modulus,

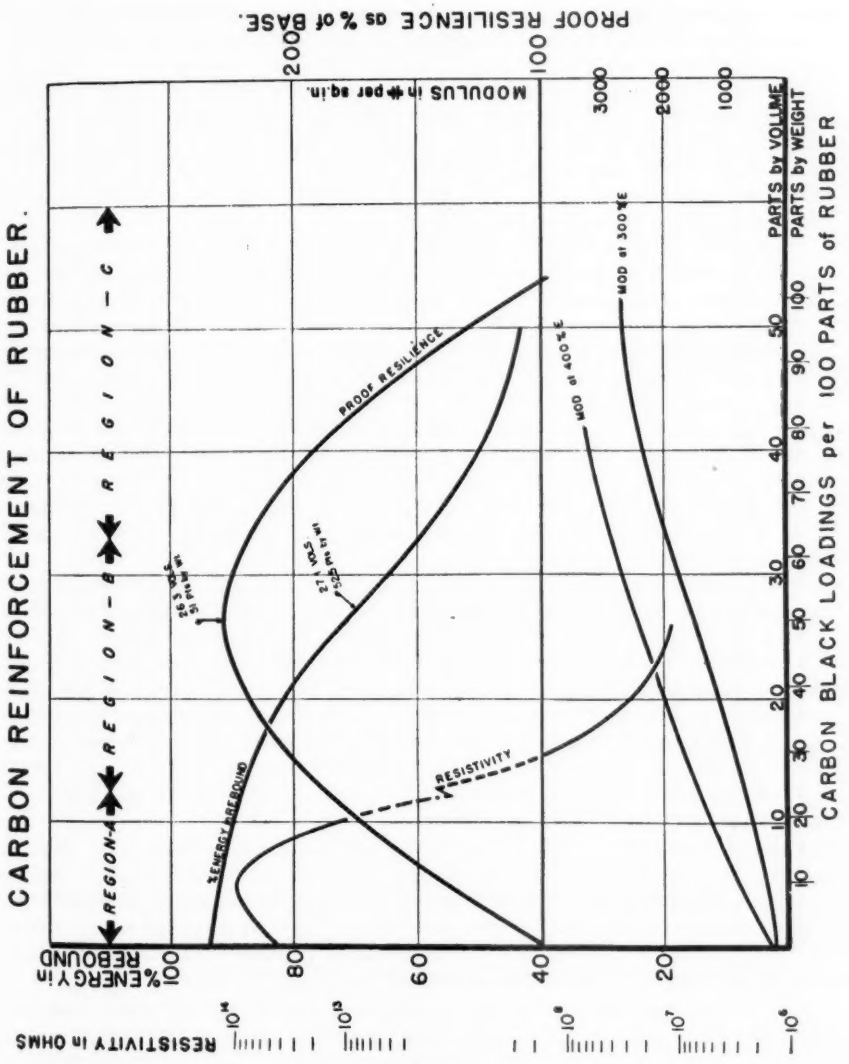

Figure 1

lower elongation, higher tensile product, higher energy. The substitution of the proper for the improper order of mixing also produces similar changes.

In order to secure maximum benefits of carbon reinforcement, mother mixings must be employed, and these should be cooled and if possible passed through tightly

set refining rolls. Evidence exists that such precautions cause marked increases in road mileage of tires, improvement in gloss of cut surface and flex-resistance of high carbon tap soles, etc. Masterbatches should be used within a month, as there is some evidence of secular changes.

Softeners should not be used in masterbatching except for a small percentage of stearic acid and pine tar (under 5 per cent on the rubber). Experience in dispersion of exceedingly finely divided "color" blacks in the paint and lacquer industry fully confirms the importance of maintaining highest viscosity conditions.

Fatty Acid usage is in a very empirical state. Many fatty acids are unsuitable because of bloom, adverse effect on rubber properties, etc. Stearic acid is still by far the most widely used, chiefly in combination with pine tar in order to retain tack. Fatty acids play a many sided role. They are essential to acceleration; they also exert a specific effect on the carbon, probably reducing interfacial tension and strengthening the rubber-carbon bond.

The dosage of fatty acid is of cardinal importance, and in the present state of knowledge should be empirically determined for each mixing, depending on the type of accelerator, dosage of carbon, and type of carbon. A very approximate rule is to add enough total acid material to coat the carbon with a monomolecular layer, plus an additional quantity, depending on the type of accelerator and on the stearic acid content of the crude rubber used. A curve is shown giving monomolecular stearic acid requirements as a function of particle size. Rubber-grade carbon requires approximately 10 per cent by weight, which for a 50 per cent tread means five parts, to which may be added 1 per cent in case mercaptobenzothiazole is used; a total of 6 per cent on the rubber in addition to that present in the crude. Of this 6 per cent one-third may be pine tar (for tack retention) and two-thirds stearic acid. Crudes containing substantially less than 1.5 per cent fatty acid require additional dosage.

Super Spectra and Royal Spectra with a particle size of 250 A. U. or less require much larger proportions for monomolecular coating (20–30 per cent by weight of fatty acid on the black). Thus compounded, Super Spectra and Royal Spectra show increased reinforcement over Micronex, thus narrowing the still unexplored "zone of optimum colloidality" to approximately 250 A. U. The trend of reinforcement between Micronex (500 A. U.) and Royal Spectra (approximately 200–250 A. U.) exhibits a flattening out which warrants the guess that particulate carbon finer than 200 A. U. will lie beyond the optimum energy absorption point, and in any case will present serious processing difficulties. All particle size data below 500 A. U. are but crude, if shrewd, estimates.

Reduced Zinc Oxide.—Take a rough rule—There must be some zinc oxide in solution together with some not in solution. Subject to this limitation, excessive zinc oxide is unnecessary. There is a tendency towards reduction to below 5 per cent on the rubber, thus leaving room for more carbon with improved wear. Values for total zinc oxide should not be reduced below 3 per cent on the rubber without careful investigation, at least in tire treads.

Selection of Proper Grade of Carbon.—Experience in the paint and lacquer industry emphasizes the intimate relationship between proper grade and details of mixing technic. The finer the particles of rubber carbon the more attention must be paid to proper incorporation. Rough rule: For wear-resistance, use the finest particle black to which you are willing to do justice in your mill room.

In evaluating rubber carbons, small laboratory experimental mill rolls (six inches) are not reliable because they impose more severe milling conditions than are used in the factory, and thus tend to iron out dispersion differences.

Laboratory abrasion testing is still in a highly unsatisfactory condition. It does not integrate all of the contributing factors. Road testing, although itself not unequivocal and statistically showing high probable error, still remains the most reliable, if also by far the most costly, test. The possibility that the high hysteresis

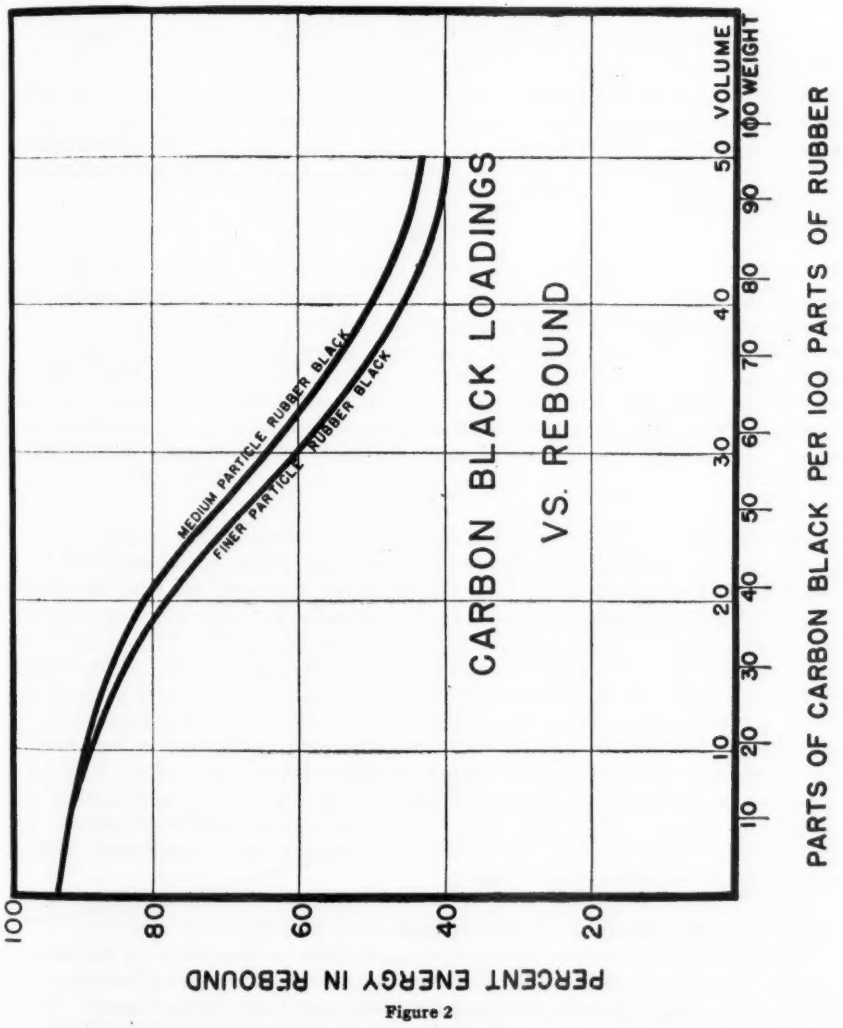

Figure 2

of carbon-reinforced treads may play a constructive role in wear-resistance will receive attention in Part II.

Tread Wear Versus Tread Cracking

The tire tread compounder of today is hard pressed between the Scylla of tread wear and the Charybdis of tread cracking. Antioxidants and anti-flexors, improved carcass and tread design, proper dispersion of carbon which has been especially

manufactured and controlled for rubber compounding, have alleviated, if not allayed, the cracking. With the solution of the cracking problem the way will be cleared for higher dosages of carbon, and so still better wear.

Part II—Its Cause

SURFACE ENERGY

No doubt exists as to the relationship between reinforcement and surface development, but the published attempts to explain this relationship in terms of surface energy or free surface energy changes are often confusing and even contradictory. It is important therefore to begin by examining the available alternatives and their implications.

Case I

Reinforcement Is Due to Increased Free Surface Energy.—This implies that the generation of a rubber pigment interface involves increased, reversible, mechanical work, and therefore that the increased work of rupture (reinforcement) as a specimen is stretched is likewise due to, and accompanied by, a progressive increase in rubber-pigment surface boundary. Such a condition has never been demonstrated, never suggested, and can scarcely even be imagined. All of the known facts regarding rubber fillers, in general, point in the opposite direction, *viz.*, a tendency towards separation of rubber from pigment, *i. e.*, a decrease in interfacial boundary.

Case II

Reinforcement Is Due to Decreased Free Surface Energy.—This implies that the generation of a rubber-pigment interface, like adsorption, is accompanied by a decrease in free surface energy, and therefore that the increased work of rupture is due to, and accompanied by, a progressive decrease in rubber-pigment interface, *i. e.*, a separation of pigment particles from their rubber matrix. At first blush this view would seem more plausible than Case I. Unfortunately, there is no experimental evidence that in the case of reinforcing pigments there is any such separation. A study of Schippel's data reveals that in the case of carbon black up to 30 volumes, and in the case of zinc oxide up to 75 volumes, the volume increases on stretching were actually less than that of the base mixing! Again, there is no proof that, even at rupture, a specimen of reinforced rubber fails at the pigment boundary. Finally, as Barron and Cotton[1] have shown, the work of rupture of carbon reinforced rubber is eighty per cent non-reversible, whereas free surface energy changes are by definition reversible phenomena.

With these considerations in mind, let us briefly review some of the published opinions on the mechanism of reinforcement.

Wiegand in 1920[2] wrote: "Schippel's results throw a clear light on the mechanism of the reinforcement action of the finer pigments. These resist increase of the free surface energy necessary to separate them from their rubber matrix. When a carbon black stock is stressed to rupture, the work done on the rubber phase must be increased by an amount representing the increase in surface energy required to separate each particle of carbon from its surrounding phase of rubber."

Here is a clear, not to say categorical, exposition of Case II—the low free surface energy concept. The writer made two assumptions, first, that failure occurs at the rubber-pigment boundary, and second, that the increased proof resilience (work of rupture) is measured by the increase in surface energy required to separate rubber

from pigment. So far as the writer is aware, neither of these assumptions has been substantiated during the intervening seventeen years.

Parkinson in 1929[3] wrote: "The larger the surface the greater is the boundary

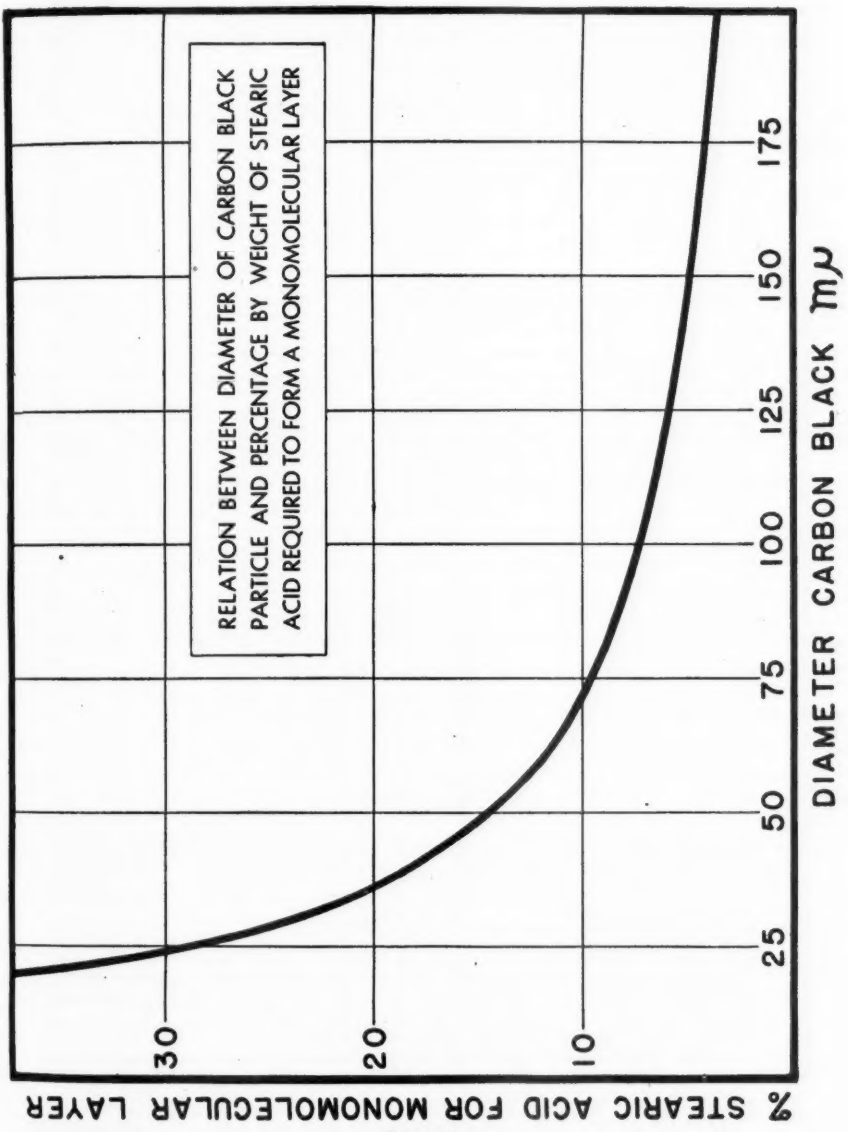

Figure 3

surface energy or interfacial tension between the filler and the rubber matrix. In addition to this, as the particles get smaller their intrinsic free energy becomes greater owing to their high degree of curvature, a greater proportion of each mole-

cule lying outside the surface, so that a greater proportion of its energy is available as free surface energy. The effect of very small particles, therefore, is to increase

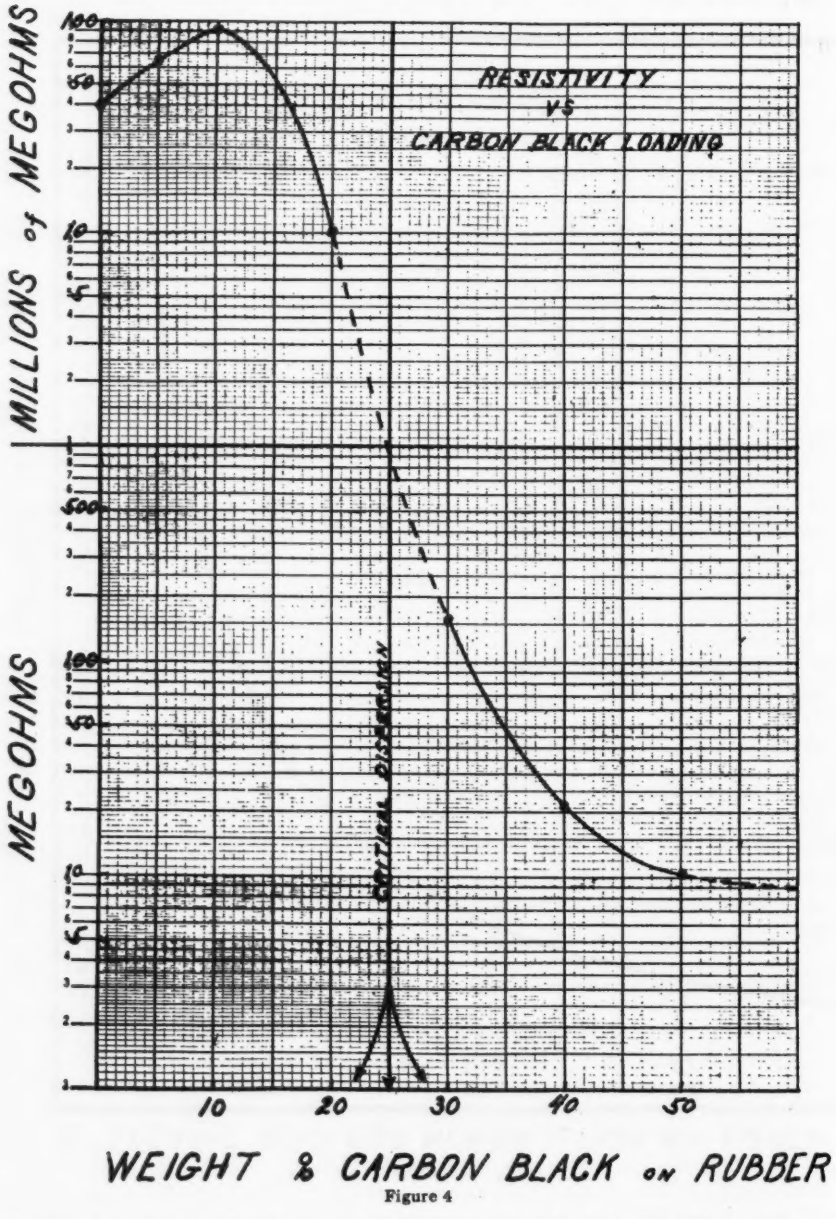

Figure 4

the free energy, not only by increasing the surface but by increasing the energy per unit area of surface."

Here we see Case I invoked. Later, the same author says: "It is considered by

some investigators that rubber itself is adsorbed by carbon black, in other words that the bond presumed to exist between rubber and filler is in the nature of an adsorptive attachment . . . ."

By this reference to adsorption, Parkinson tacitly changes over to Case II, the opposite condition to Case I, and to make his position completely impregnable he shrewdly adds: "To say that a filler reinforces because its particles possess a large amount of free surface energy is no explanation at all, but the idea provides a basis from which, as knowledge progresses, it may be possible to build up satisfactory theories on what appears to be a complicated phenomenon."

Cotton in 1930[4] wrote: "The weight of available evidence indicates that the valuable properties imparted by reinforcing fillers are directly attributable to the increase in surface energy of the compound." And again: "The work of rupture has to overcome (*a*) forces of adhesion, (*b*) the interfacial tension, (*c*) friction between flocculated particles of filler, (*d*) plastic flow around the filler particles."

There would seem no question as to the validity of items (*c*) and (*d*) mentioned by Cotton. However, when Cotton asks us to believe that the work of rupture is called upon at the same time to overcome the forces of adhesion and, their opposite, the interfacial tension, we are placed in a serious quandary. The interfacial tension acts to decrease the rubber-pigment interface which the forces of adhesion seek to prevent. Under such circumstances the natural thing for the work of rupture to do would seem to be to stand aside and allow (*a*) to overcome (*b*), or *vice versa*.

Lefcaditis[5] gives his views as follows: "On reinforcement by a filler such as carbon black, for which a multitude of facts indicates high attractive force towards rubber, the increased work required for the extension of the compounded rubber to rupture is consumed to overcome (1) the high free surface energy of the system, which is opposed to separation of the two phases, and (2) a component which will be assumed of complicated nature." Here again we note the use of the high free surface energy hypothesis, without regard to its implication. A high free surface energy would not be opposed to a separation of the two phases, but would on the contrary permit it.

Our final quotation is from the latest text-book on rubber technology by Hauser.[6] (The translation is by the writer.) "The explanation of the phenomenon (reinforcement) would then be as follows. The development of such a surface requires work which, *inter alia*, must be exerted against the surface tension of the rubber, *i. e.*, its natural tendency to diminish its surface. A part of this work is stored up in the form of reversible free surface energy. During the rupture of the reinforced specimen, on the other hand, the interfacial boundary between rubber and filler must be dissolved, and so additional mechanical work must be done."

Here we have an example of the high free energy assumption being invoked simultaneously with conditions requiring the low free energy assumption. In other words we are told that a part of the work required to generate the pigment interface will oppose its dissolution.

So much for what might be called the speculative use of the surface energy concept.

THERMODYNAMICAL STUDIES OF HOCK AND HIS CO-WORKERS

Though also accepting the view that the reinforcement of rubber with fine pigments is a function of the free surface energy, it stands to the credit of Hock that he sought to apply quantitative thermodynamical methods to this study. Reduced to simplest terms, the essence of Hock's method of attack was as follows. The heat of wetting of rubber in, for example, benzine being known; and the heat of wetting of carbon black also being known—an unvulcanized compound of rubber and

carbon black was permitted to swell and the heat tone determined. The extent to which the heat tone differed from the algebraical sum of the heats of wetting of the two components was taken as a measure of the total energy required to separate rubber from pigment. This was then calculated back to unit content of reinforcing pigment. Hock calls it Heat of Adhesion or "Heat of De-Wetting."

Initial results seemed promising. It was found that heat absorption occurred during the swelling of the rubber-carbon black mixing and, when calculated back, an order of magnitude agreement was obtained with values for resilient energy taken from Wiegand's papers.

There are, of course, many sources of error and doubtful points of interpretation in such a method of attack, and it is only fair to Hock to say that he himself has recognized practically all of them in his 1934 paper.[7] In order to facilitate discussion, Hock and Hartner's data for carbon black have been recalculated. All energy values have been reduced to the same units and the course of the reinforcement, or A function, for carbon black referred to the same abscissa as the various heat tone values obtained. The following points require mention:

(1) The course of the heat of adhesion values as calculated by Hock does not in any way conform with the trend of the A function.

(2) The values for heat of adhesion do not conform even in order of magnitude with those actually obtained in the reinforcement of rubber with carbon black.

(3) Pure rubber itself can show secular changes in the amount of heat absorption incurred during swelling, which are greater than any of the heat tone effects obtained in the experiments.

(4) The calculation of "heat of adhesion" from the algebraic sum of the heat of wetting of the rubber and that of the carbon black involves the assumption that the carbon black has been severed from the rubber and completely wetted by the solvent. This would scarcely seem warrantable in view of the experiments of Stamberger, Goodwin and Park, Menadue, Boiré, and others, which indicate that the bond between rubber and carbon black is stronger than that between either rubber or carbon black and the solvents customarily employed.

(5) The approximation of the heat tone of the compounded rubber to that of the rubber alone, except for slightly higher values, taken in conjunction with the still higher values shown for crude rubber which has been allowed to recover after milling, and taken also in conjunction with the well-known setting up effect of carbon black on crude rubber and on reclaimed rubber[8] which has been heavily milled, suggests that the positive heat tone of the rubber-carbon black compound when swelled in benzine may have been due not to the dissolving of the rubber-pigment interface, but to a change in the rubber phase, through the instrumentality of the carbon black in which might be termed an "accelerated recovery effect."

(6) Finally, there is of course the difference between uncured and cured mixings, to say nothing of the ever present doubt as to whether the work of rupture is even remotely related to dissolution of the rubber-pigment interface.

In the writer's opinion, both the experimental technic and the thermodynamical method of approach of Hock and his pupils are in themselves sound. Their work ought to be supplemented by additional experimental determinations under varied conditions, and the final results correlated, not with the values for the initial work of extension of reinforced rubbers, but with reversible energy values obtained under "dynamic" conditions.

This brief review of surface energy theories in relation to rubber reinforcement will serve to illustrate the unsatisfactory state of our knowledge.

The Work of Incorporation

It would appear that apart from confusion as to sign in the expression "high free surface energy" and a failure to recognize its implications, there has been also a persistent tendency to equate, at least in part, the mechanical work of incorporation of a pigment with the free surface energy of its newly acquired rubber boundary.[8]

There is no evidence that they are even remotely related. In a tire tread the incorporation of one pound of carbon black in two pounds of rubber necessitates spreading this unvulcanized rubber over approximately ten acres of surface. From the moment any of the carbon black particles have been dispersed, reinforcement has already begun even in the uncured rubber; thus as mixing proceeds the viscosity progressively increases as the zones of reinforced rubber extend throughout the whole matrix.

The more efficient the reinforcing action of any particular grade of carbon black in vulcanized rubber the greater is found to be its stiffening action on the raw stock. Thus in the opinion of the writer, the increased work of incorporation of reinforcing pigments may be simply, if prosaically, explained. It has raised the entropy of the universe in the form of frictional heat!

We turn now from surface energy to some other aspects of reinforcement theory.

MECHANICAL REINFORCEMENT

The Schippel Effect

Any discussion of the mechanical features of reinforcement must begin with a consideration of whether or not rubber and pigment remain united. Schippel showed that the coarse, non-reinforcing pigments developed large volume increases in stretched rubber, and later investigators confirmed microscopically his deductions as to the presence of vacuoles. Clearly where the rubber pulls away from the pigment particles the latter can play no positive role in reinforcement, and can only detract from physical properties by virtue of dilution and also, depending on their crystal habits, by the cutting effect brought about during lateral contraction, thus hastening rupture.

Schippel's data confirm the permanence of the bond existing between rubber and such reinforcing pigments as carbon black, lampblack, and zinc oxide. The absence of volume increase with exceedingly fine pigments may, however, be regarded as in some measure due to diminished stress.[9] It is also to be noted that iron oxide showed a volume increase practically as low as that for carbon black and that Schippel states that lampblack showed an even smaller volume increase than carbon black. The facts can perhaps be summarized in the statement that the absence of vacuole development or of volume increase is a necessary but not a sufficient condition of reinforcement.

Solid Film Theory—Spear[10]

Postulating the adsorption of rubber on the surface of the carbon particles, Spear first points out that the portion of the rubber on the immediate surface of the carbon ought to have less extensibility than the original rubber, also that the total elongation of the mass would be less than if pure rubber only were present because a considerable portion of the distance is taken up by the particles of the compounding materials.

Spear then explains that: "According to the plastic solid film theory, the films between the solid particles of carbon black are much more resistant to distortion than the matrix would be were no compounding ingredient present. This explains at once why the mass is stiffer and why the curves for carbon black stocks partake

very nearly of the nature of straight lines. Even for low elongations these films are thin enough to become operative, whereas in the case of pure gum stocks, the stretching process must proceed a considerable distance before the matrix is thinned sufficiently to form effective films. Finally, these films are very strong, hence we should expect the ultimate tensile of carbon black stocks to be high, which is, of course in accordance with the facts."

Wiegand, in discussing Spear's theory[11] alludes to its attractive features but draws attention to irregularities such as lithopone. To this might be added certain striking differences between pigments of similar particle size such, for example, as P-33 and Shawinigan, Fumonex, or lamp black, all of which are in the same general range of particle size (between 0.1 and 0.2 μ) but which differ basically in reinforcing behavior.

In all probability, the Spear effect makes itself felt to some extent in all reinforcement phenomena, subject, however, to important differences depending upon surface activity and particle shape.

Stress Distribution.—Wiegand[11] has pointed out that, provided anchorage between pigment and rubber is complete, there will be continuity of stress, the lines of stress going through each particle instead of around it; also the uniformity in pigment particle size will result in a balanced state of stress throughout the rubber matrix, thus preventing any piece-meal type of failure which would tend to shorten the stress strain curve.

Shape of Particle.—The effect of differing particle shapes has been discussed by various writers. A suggestive mechanical analogy has been described by Barnett[9] whose conclusions, which are all of course based on the assumption of complete anchorage, are as follows:

"(1) Stresses are greater at the surface of large particles than small ones, thus explaining the Schippel effect.

(2) The stress in the vicinity of a rectangular particle is great if the particle is oriented with its length parallel to the direction of the pull, but small if oriented normal to this direction.

(3) The addition of pigment causes the strain on considerable of the rubber to be raised to the stiff part of the stress-strain curve, when the average rubber would normally be in the soft part of the curve."

Wiegand[12] cites the stiffening action obtained by means of $^1/_{16}$" ground fibers, and points out that a pure gum mixing containing fiber shows a stiff curve at the outset, which later collapses. Clearly, during the early part of the curve each fiber anchored or immobilized some of the rubber, but was later unable to maintain the anchorage. He pointed out also that anisotropic ingredients such as talc and clay, plaster of Paris, etc., could be regarded as acting in a similar manner excepting that, since the particles were of various sizes and lengths, the sharp discontinuity in the fiber stress-strain curve would disappear. Instead there would be a stiffening effect throughout the curve.

He also suggested that some such condition might be the explanation of the inferior reinforcing properties of lamp black despite its marked stiffening action, and that, in general, particle shape might explain the behavior of these pigments which stiffen markedly and yet show low resistance to tear.

This brief review of the mechanical aspects of reinforcement has been included with no intention of attaching to them any enhanced importance. It would, however, seem salutory in the deeper consideration of true reinforcement to keep in mind the nature and extent of those physical changes which may be ascribed to mechanical forces as distinguished from colloidal and molecular forces.

Need for a New General Reinforcement Theory.—It has already been pointed out that surface tension forces, although widely invoked since 1920 by various investigators, have not provided any convincing picture of the *modus operandi* of reinforcement of rubber. So far as the writer is aware, there is not the slightest evidence to indicate that, during the extension to rupture of properly reinforced rubber, progressive changes in the pigment-rubber interfacial boundary occur at all. In these circumstances it would seem idle to attempt to equate purely hypothetical changes in free surface energy with energy absorption values which are in a preponderating degree non-reversible.

* * *

Any new concept of the structure of reinforced rubber would be expected to shed at least some light on the outstanding features which still stand in need of explanation. Some of these will now be listed.

POINTS REQUIRING ELUCIDATION IN ANY NEW GENERAL THEORY OF REINFORCEMENT

(a) General Trend of Reinforcement

Course and character of energy—loading curve.

Early maximum occurring long before the calculated limits of pigmentation based on considerations of piling.

(b) Detailed Feature of the Loading Curve

Regions A, B, and C. Solubility of uncured reinforced mixings.

(c) The Properties of Various Soft Carbons—Effect of Surface Chemistry

(d) The Properties of Other Reinforcing Powders

OUTLINE OF NEW REINFORCEMENT THEORY

On the assumption of a continuous phase of rubber, the tetrahedral piling of the pigment phase would result in the theoretical possibility of loading 300 volumes of pigment to 100 volumes of rubber, or in the case of carbon black approximately 600 per cent by weight on the rubber. Such proportions have never been even remotely approximated. Calculations also show that in a 50 per cent tread stock the interparticle distance would equal one radius, or 25–30mμ, which is one-fifth the estimated minimum diameter of the masticated rubber macromolecule. These facts illustrate the need for revision of existing theories.

* * *

We therefore begin by:

(1) The replacement of the existing assumption of a system composed of a reinforcing pigment constituting the dispersed or discrete phase immersed in a continuous phase of rubber by the view that the rubber phase is also discrete, and consists of structural units (macromolecules) larger in general than the individual particles of reinforcing carbon.

(2) The association of reinforcing particles with the rubber macromolecules in what may loosely be termed a new molecular complex possessing altered chemical and physical properties compared with pure rubber.

(3) With respect to carbon black reinforcement, the attachment of single layers of carbon particles around each rubber macromolecule, these particles also functioning as bonds between adjacent macromolecules.

(4) The possibility of the disposition or packing of a limited additional proportion of carbon particles in the "voids"* between the rubber units.

(5) The "voids" having been filled, the incorporation of additional quantities of carbon black will entail gradual wedging apart of the rubber units, with progressively diminishing reinforcement.

APPLICATION OF NEW THEORY

(a) General Trend of Carbon Reinforcement

TABLE I

NEW REINFORCEMENT THEORY

(1) Assume: Rubber the Discrete Phase—Spherical Habit—Tetrahedral Piling—Rubber = 74 Volumes—Voids = 26 Volumes

	Volumes	Parts by Wt.	R = 100 (Wt.)
Rubber } 74 Vols.	73	67.9	100
Sulfur (3%) } 74 Vols.	1		3
Zinc Oxide (1% Soluble)	0.15		
(4% Pigment)	0.5	2.8	5
Carbon Black (No Fines), 74% of 25.5 Vols.	18.87	33.96	50.01
Stearic Acid (Fixed at 4%)	2.9	2.72	4.0
Accelerator (1% Mercapto)	0.5	0.679	1
Antioxidant	0.6	0.679	1
Pine Tar (Balance)	2.35	2.54	3.75
	99.87		167.76

(2) Assume Further: Zinc Oxide—3% (1 Soluble, 2 Pigment)—25% of Carbon Black Voids Filled with Its Own Fines

	Volumes	R = 100 (Wt.)	
Rubber } 74 Vols.	1	3	
Sulfur (3%) } 74 Vols.	73	100	
Zinc Oxide (1% Soluble, 2% Pigment)	0.36	3	
Carbon Black	20.93	55.6	
Accelerator	0.48	1	
Antioxidant	0.57	1	
Stearic Acid (Fixed at 4%)	2.88	4 }	5.24
Pine Tar (Balance)	0.78	1.24 }	
Total	100.00	168.84	

N.B.—Softener to Black Ratio Now 9.5%.

In Table (I) there is illustrated the application of the theory to a tire tread reinforced with carbon black. The calculated position of the maximum appears to fit in well with the empirical optimum loading (50 to 55 per cent on the rubber).

(b) Regions A, B, and C of the Energy-Volume Loading Curve

Region A.—In the case of reinforcing carbons we picture the attachment of a single layer of carbon particles around each rubber macromolecule as presenting no free carbon particles. The new molecular complex of carbon and rubber is being built up in direct proportion to the addition of carbon black, thus accounting for the rapid and approximately linear rise in energy with volume loading in this region.

The bound condition of the carbon explains the excellent electrical resistivity

* These voids are not pictured as preëxistent, but as developable during the progressive incorporation of reinforcing pigments such as carbon black. The rubber macromolecules are assumed to be deformable.

and break-down properties in Region A. The absence of friction between free carbon particles accounts for the relatively high rebound resiliency and "liveliness" of compounds containing 12 per cent or less by volume of carbon black.

Region B.—As we pass into this region through the incorporation of additional carbon black the first is complete saturation as regards the mono-particle layer, accompanied by the increasing presence of carbon which is not bound or chemically combined with the rubber, and which tends to fill the voids or interstitial spaces. The presence of this "free" black causes an immediate and sharp drop in the electrical resistance properties, and adversely affects rebound resilience, while at the same time the rate of increase of energy absorption or "proof resilience" declines.

At the point where sufficient carbon has been added to fill the interstitial spaces but no more, we have reached, at least approximately, the maximum of the energy curve. The reason for this maximum is the coexistence of maximum bond or attraction between the rubber units which are cemented together with a mono-layer of carbon, and the frictional resistance of the free carbon particles present in the interstitial spaces, which of course adds to the (non-reversible) absorption of energy.

We thus account for the coexistence in carbon reinforced rubber of high hysteresis, low rebound resilience, relatively high Durometer hardness, and at the same time maximum wear and tear resistance.

Indeed, far from considering the low rebound and high hysteresis of carbon reinforced treads at the optimum portion of Region B as an unmitigated evil, the writer ventures the opinion that, at least in pneumatic tire treads, the low rebound resilience, or relatively high capacity to degrade energy into heat, may actually improve road wear. Whereas in the case of a perfectly resilient tread the rear section of a non-skid button would be subject to the law of action and reaction, what actually occurs in the case of a carbon black tread is that the "kick-back" as the button leaves the road is reduced in intensity by approximately 40 per cent, thus reducing "wiping" and cupping.

Also in Region B the attainment of complete encasement of the rubber units in a layer of chemically bound carbon black would be expected to cause a sharp decrease in the solubility of the unvulcanized mix.

Region C.—The addition of carbon black in amount greater than that required to fill the voids (approximately 25 volumes) results in wedging apart to an increasing degree the structural units of rubber with their surrounding envelopes of carbon particles. From this point on, the increase in frictional resistance is no longer sufficient to offset the decreasing cohesive strength, and reinforcement progressively declines.

The extraordinary range of Region C in the case of carbon black, characterized by comparatively high values for tensile strength and elongation, at loadings which have already produced a hardness and plasticity of leather-like character, may be understood in terms of the close packing possible in the case of an exceedingly fine pigment of this kind, thus minimizing the separation of the rubber structural units. Conditions of uniform stress would manifestly be impossible in the case of heavy over-loading with pigments consisting of irregularly shaped particles larger than the rubber macromolecules themselves.

(c) The Properties of Various Carbons—Surface Chemistry

In so far as reinforcement is concerned, it would appear that the presence of a certain as yet undefined minimum of combined oxygen on the surface is essential to intimate bonding with the rubber. Carbon pigments may therefore be divided into those with active and those with inactive surfaces.

The lampblacks, including natural gas varieties of this general type such as Fumonex and Gastex, are intermediate in regard to surface activity between the impingement carbons and the thermal decomposition carbons. They are also larger in particle size and probably of elongated habits. They would therefore be expected to have a shorter reinforcing range because of their being too large to pack within the interstitial voids. They will show high modulus partly because of particle shape (mechanical reinforcement) and partly because of surface activity (chemical reinforcement). The presence of a considerable proportion of particles larger than the rubber macromolecules will clearly shorten the stress-strain curve and diminish tear, but provide improved rebound resilience and less hysteresis because of diminished inter-particle friction.

Finely divided thermal carbons such as P-33, having an inactive surface and a high degree of uniformity, will be expected to pack well, to show a wide range of loading capacity, will show no tendency to form a new molecular complex, and so will leave the stress-strain curve substantially unaltered. There being a minimum of interference with the rubber structural units, the elongation is excellent, also tear resistance. Mechanical reinforcement through the development at high elongations of plastic solid films may also play some role as regards tensile strength.

If, with no other change, the surface of such a black could be rendered active through the presence of oxygen compounds, one would expect a rise in modulus and a decrease in elongation. That such, indeed, happens is indicated by Spear.[13]

Inert carbons of particle size larger than that of the macromolecule of rubber would be expected to pack relatively poorly, to separate the rubber units, to contribute to cutting action at the stage of intense lateral compression, and so to bring about shortening of the stress-strain curve. These carbons are illustrated by Thermax and Velvetex. Compounds made from such carbons are, of course, highly resilient.

It may here be pointed out that according to this theory there must be certain compensations among reinforcing pigments. A maximum of tensile strength, for example, cannot be expected to coincide with maximum rebound resilience. Conversely, reinforcing pigments which are too large in particle size to pack interstitially, and which are therefore wedged between the rubber structural units, will always tend to show low hysteresis effects. They are literally "mounted in rubber."

Also, on this theory, relatively high hysteresis and low rebound emerge as inherent or structural concomitants of perfect reinforcement, at least as defined in terms of energy adsorption and wear resistance.

(d) Other Reinforcing Powders

The explanations already given with regard to different shapes and sizes of carbon particles would seem capable of application to other compounding ingredients. The two cardinal considerations according to this theory are: (1) the activity of the surface *vis à vis* the rubber substance, which evaluates their capacity for true or molecular reinforcement, and (2) the size and shape of the particles, which influence their packing and distribution among the macromolecules of rubber.

In proportion as they are lodged, not interstitially but between the rubber structural units, they diminish resistance to wear and tear, improve the rebound resiliency, but shorten the effective (reinforcing) loading range.

The theory here roughly sketched can in no sense claim completeness. It may, indeed, be found incompatible with many facts. Some of the points requiring further analysis and study are:

(1) The effect of continued mastication, with diminishing molecular weight,

upon the course of reinforcement, with particular reference to particle size and to the position of the energy maximum.

(2) The effect of elongated shape of the rubber macromolecules upon the voids calculations.

(3) The effect of the mono-particle layer assumption upon the voids calculations.

(4) The location of various softeners and non-pigment ingredients between the rubber phase and the pigment-in-voids phase.

(5) The theoretical analysis of tear phenomena in relation to the "discrete-rubber" theory.

The writer's reason for propounding the "discrete-rubber" theory of rubber reinforcement at this time is that for upwards of a year he has found it a more convenient way of viewing the known facts, and that it has already to some extent been found useful in fields other than rubber, where high molecular weight vehicles are combined with colloidal carbon. He therefore hopes that where it may not solve, it yet may stimulate.

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Change of Volume of Rubber on Stretching: Effects of Time, Elongation, and Temperature

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I. INTRODUCTION

The present investigation was suggested by the work of Davey and his students,[1] who found that a time lag of a few seconds elapsed between the stretching of rubber and the development of the full intensity of the x-ray diffraction pattern. Feuchter[2] had previously shown that the volume of rubber decreased on stretching, and on the basis of these two observations one of the present authors predicted that a time lag would occur in the change of volume of rubber on stretching. When this time lag was looked for, it was found without difficulty,[3] and seems to afford a simple, convenient means for studying the fibering or "crystallization" of stretched rubber. Incidental to studying this time lag, observations were made on the effect of composition, temperature, and elongation on the volume of stretched rubber.

The time lag has been recently observed in connection with the double refraction of stretched rubber, by Thiessen and Wittstadt,[4] and probably constitutes the effect which was dismissed by previous observers as "optical creep."[5]

The literature on rubber contains a wide range of values for the change of volume on stretching and for Poisson's ratio. Most of the data pertain to rubber-filler systems,[6,7] which increase in volume on stretching because the formation of vacuoles around the coarse filler particles or aggregates increases the volume of the stretched rubber to a much greater extent than the fibering of the rubber phase decreases it.

Early investigators[8] who worked with rubber containing no fillers failed to observe any decrease in volume on stretching, probably for the reason that inhomogeneities such as sulfur crystals due to the relatively high percentage of sulfur used at that time led to the formation of vacuoles which masked the effect of fibering of the rubber phase.

II. PREPARATION OF SAMPLES

The samples used in the present investigation were molded rings, which were made as thin as practical in the radial dimension so that when they were stretched the inside and the outside would have nearly the same elongation. The rings were approximately 1 mm. in width, 4 mm. in depth, and 100 mm. in average circumference. The inside circumference was about 96.9 mm. and the outside, 103.1 mm., hence when the rings were stretched by a relatively large amount the actual elongation of the rubber ranged from about 3 parts per 100 below to 3 parts per 100 above the average elongation, which is the figure reported in the present work.

The mold used for making the rings consisted of a heavy metal plate containing cylindrical cavities. In each cavity a removable disc, 1 mm. smaller in radius than the cavity, was fitted in such a way as to leave an annular space in which the ring was molded. By taking out this central disc, a sample which had been vulcanized in the cavity could be removed without damage. Details of the mold are shown in Fig. 1.

The rings, after vulcanization, were carefully trimmed and inspected for flaws and inclusions before use. Those which were to be employed in the mercury-filled dilatometer were stored under mercury for some time to remove free sulfur and other components which might cause fouling.

Most of the work reported in this paper was done with two "pure gum" compounds, which were vulcanized with mercaptobenzothiazole and tetramethyl-

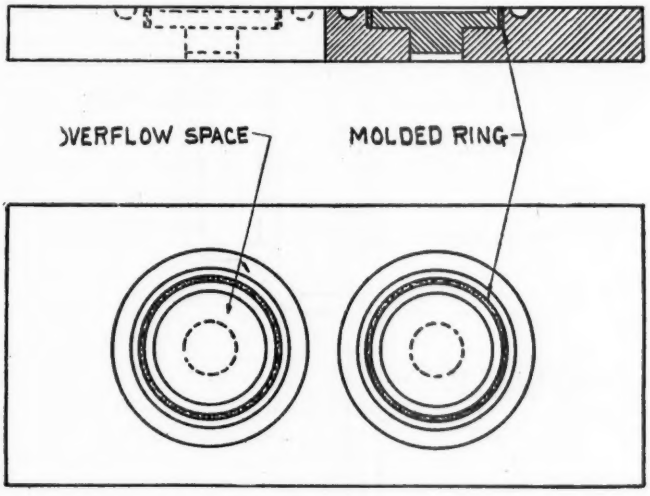

Figure 1—Mold for Rubber Test Rings

thiuram disulfide, respectively, as accelerators. These are compounds *I* and *II* in Table I. Compound *II* is identical with compound *B*, which was used in photoelastic studies on rubber. A few experiments were conducted with compounds *III* and *IV*, which contain 10 per cent by volume of whiting and carbon black, respectively.

METHODS OF MEASURING VOLUME CHANGE

Some preliminary measurements of the change of volume of rubber on stretching were made by the method of hydrostatic weighings. Rubber rings of known vol-

TABLE I

COMPOSITION OF RUBBER COMPOUNDS

Ingredients	Compounds[a] (Parts by Weight) I	II	III	IV
Smoked sheet rubber	100	...	100	100
Pale crepe rubber	...	100	...	...
Zinc oxide (Kadox)	1	1	5	5
Stearic acid	1	1	1	1
Mercaptobenzothiazole	1	...	0.8	0.8
Tetramethylthiuram disulfide	...	0.3	...	...
Sulfur	2	2	3	3
Whiting	...	...	34[b]	...
Carbon black (Micronex)	...	...	...	22.5[b]

[a] Compounds *I*, *III*, and *IV* were vulcanized for 30 minutes at 141° C., and compound *II*, for 30 minutes at 126° C.

[b] 10% of the volume of the compound.

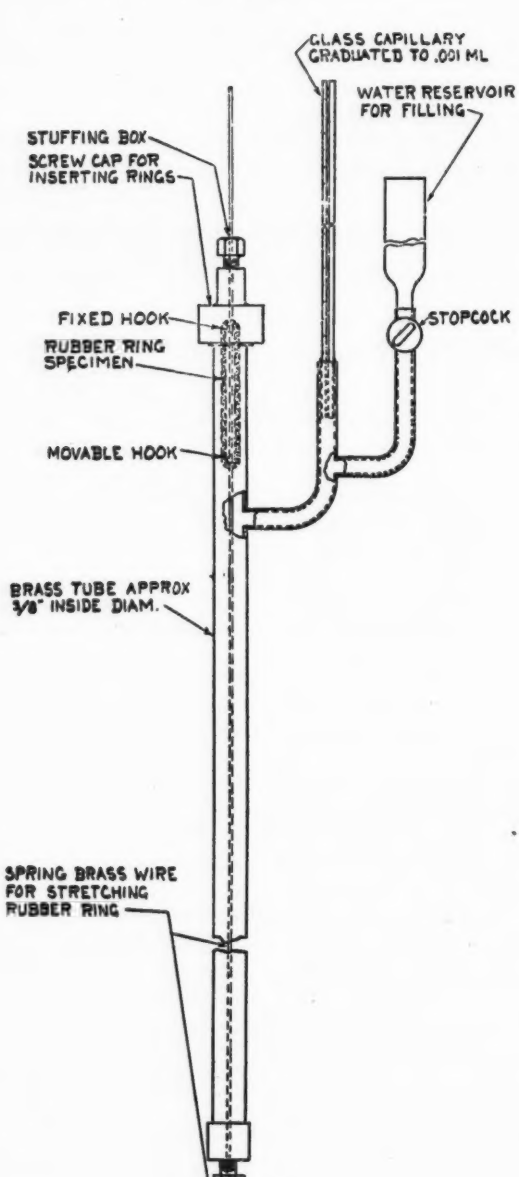

Figure 2—Water-Filled Dilatometer for Measuring the Change of Volume of Rubber on Stretching

ume were placed on a stainless steel frame, and were weighed in water, first in the unstretched condition, and then at intervals after stretching. The change of volume with time could be followed by observing the change of weight. This method, however, was not followed for the measurements here reported because it was not practical to make weighings within a few seconds after stretching, as was desired; furthermore, at long time intervals the results were rendered uncertain by the absorption of water by the rubber.[10]

The measurements at short time intervals were made with a dilatometer, in which water or a salt solution was used as the containing liquid, while measurements at long time intervals were made with a mercury-filled dilatometer.

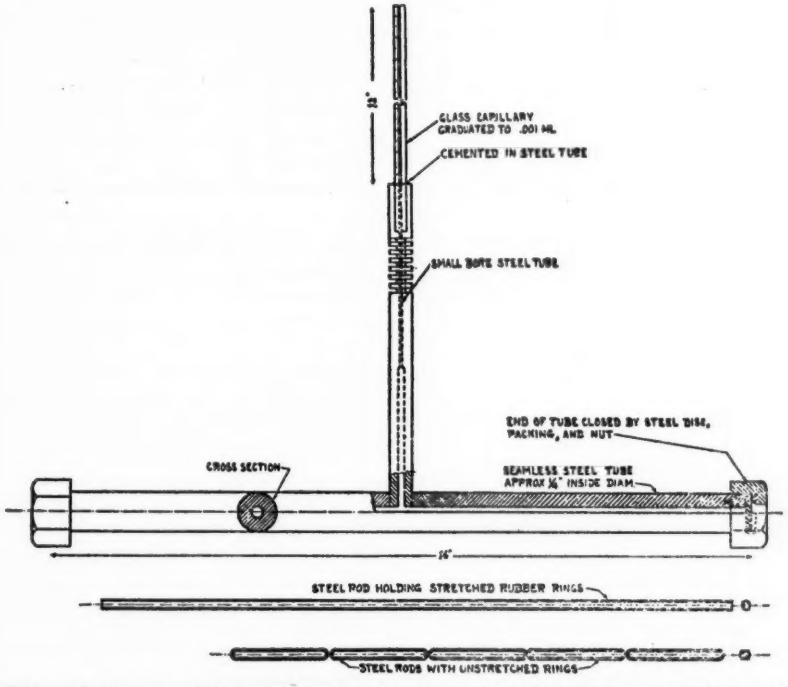
GLASS CAPILLARY GRADUATED TO .001 ML
CEMENTED IN STEEL TUBE
SMALL BORE STEEL TUBE
END OF TUBE CLOSED BY STEEL DISK, PACKING, AND NUT
CROSS SECTION
SEAMLESS STEEL TUBE APPROX ¼" INSIDE DIAM
16"
STEEL ROD HOLDING STRETCHED RUBBER RINGS
STEEL RODS WITH UNSTRETCHED RINGS

Figure 3—Mercury-Filled Dilatometer for Measuring the Change of Volume of Stretched Rubber over Long Periods of Time

Water-Filled Dilatometer for Measurements at the Shorter Time Intervals

The apparatus which was used in measuring the change of volume at intervals from a few seconds to 20 or 30 minutes after stretching is illustrated in Fig. 2. It consisted essentially of a brass tube about $^3/_8$ inch in diameter and 20 inches in length, connected by a side arm to a calibrated glass capillary tube. The brass tube was provided with stuffing boxes at each end, through which a 1-mm. brass wire could be drawn back and forth. A ring-shaped sample could be stretched within the tube by means of a fixed hook attached at one end of the tube and a movable hook fastened to the brass wire.

In using the apparatus one or more rubber rings were mounted, unstretched, over the two hooks; the tube was then closed and filled with water or a salt solution to

a convenient height on the glass capillary. The filling was facilitated by a second side tube which was provided with a stopcock. When the rubber rings were stretched by drawing the brass wire through the tube any change in the volume of the rubber was indicated by a change in height of liquid in the capillary. Control experiments in which the brass wire was drawn through the tube without a sample

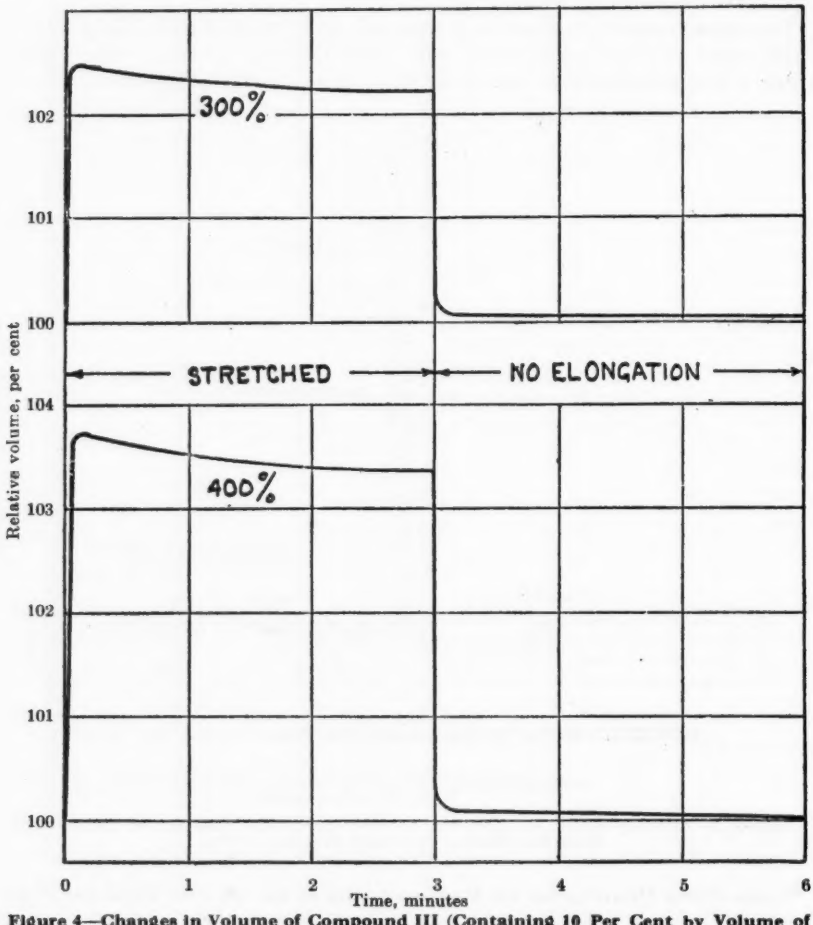

Figure 4—Changes in Volume of Compound III (Containing 10 Per Cent by Volume of Whiting) when Stretched and when Released

attached showed no appreciable motion of the liquid in the capillary, thus indicating that the stuffing boxes were tight and that the brass wire was uniform.

The dilatometer was, in most circumstances, very sensitive to temperature changes, so it was mounted in a well-insulated water bath which was provided with means for temperature control. Since, however, some fluctuations in temperature were unavoidable, a second dilatometer like the first, except that the stretching mechanism was absent, was mounted in the water bath, and afforded a direct means of correcting the observations for slight changes in temperature.

No account was taken of any increase in volume resulting from heat generated by the stressing of the rubber, since it seemed probable, from the dimensions and shape of the instrument, that most of this heat would be dissipated to the water bath in a very few seconds. But even if the heat had been confined to the dilatometer, the resulting increase in volume would under most circumstances have been considerably less than the decrease caused by fibering. During the stretching of a sample it was possible to observe, in some instances, a slight upturn of the volume just an instant before the fibering of the rubber caused a sharp decrease. This momentary upturn is indicated on the curves shown in Fig. 6, which relate to observations at 25° C. Similar measurements at 0° C., however, showed no upturn, probably because the heat generated by stressing the sample was transferred almost instantaneously to the confining water which, at that temperature, had a coefficient of expansion practically equal to zero.

The glass capillaries used in the earlier part of the investigation were made from selected capillary tubing, and were calibrated in the usual manner. Later it was found more convenient to use capillary pipettes of the Kahn type which were graduated to 0.001 cc. over a range of 0.200 cc.

In most of the work with the water-filled dilatometer the readings were made visually at intervals of 5 seconds or more, but in some experiments observations were recorded photographically on motion picture film at intervals of about 1 second. The apparatus was so arranged that the field of view included the capillary tubes, a stop-watch, and a tape graduated in percentage elongation and connected to the brass wire used for stretching the sample.

When it was found, from observations made by hydrostatic weighings that the swelling of stretched rubber might be different from that of unstretched rubber, the water which had been used as a confining liquid was replaced by a saturated salt solution to minimize the amount of swelling. The results obtained with the salt solution were not significantly different from those previously obtained with water alone, for time intervals up to 20 minutes. The possibility that significant swelling might occur even with salt water, together with the possibility of slow leakage through the stuffing boxes, rendered it desirable to use a different type of apparatus for measurements over periods of days or weeks, and the mercury-filled dilatometer was developed for this purpose.

Mercury-Filled Dilatometer for Measurements at the Longer Time Intervals

The dilatometer in which mercury was used as a confining liquid is shown in Fig. 3. It consisted essentially of a heavy steel tube, closed at the ends by means of lapped steel discs, and connected through a steel capillary tube to a glass capillary. When the steel discs were lubricated lightly with stopcock grease and held securely in place by screw caps, no leakage was observed under either vacuum or pressure. The steel capillary tube was provided with fins, as indicated in the figure, so that when the dilatometer was used at an elevated temperature the cemented glass-to-metal joint did not become hot enough to soften.

Two methods were used for stretching the rubber rings. When the temperature at which the experiment was to be conducted differed appreciably from that of the room, the rubber rings were slipped over hooks and placed, unstretched, in the steel tube. This was then brought to the desired temperature in an appropriate bath, after which it was removed quickly and wrapped in cloth to minimize temperature change. The rings were then stretched and the hooks fastened at the ends of the tube. When the temperature employed was that of the room the samples were stretched over a rod which was then slipped into the dilatometer tube.

The dilatometer tube, with the sample in place, was closed by means of the lapped steel discs, and was placed in a constant-temperature bath. The air was then evacuated through the capillary, and the whole filled with mercury by means of a two-way stopcock to an appropriate height in the capillary. This operation, from the time the sample was stretched, required about 20 minutes, so the experiments with the mercury-filled dilatometer served to indicate only that part of the volume change which occurred after the 20 minutes. In order to obtain the total volume change, the portion which occurred during the first 20 minutes was obtained by means of the water-filled dilatometer described in a preceding section.

Tests were always made with duplicate mercury-filled dilatometers, one containing unstretched, and the other, stretched rubber. The rubber samples, which weighed about 1.2 grams, were selected so as to have the same weight to within 1 mg., and the hooks or rods used for stretching or mounting the specimens were adjusted so that their weights were equal to within 1 mg.[11] Small differences in the volumes of the dilatometers were adjusted by introducing the requisite amount of steel into the larger of the two. By using this technic the differences in the readings of the dilatometers containing the stretched and the unstretched rubber, respectively, represented within a small experimental error the change of volume due to stretching, and the computation of the results was thereby greatly simplified.

FACTORS INFLUENCING CHANGE OF VOLUME

The decrease in volume of rubber on stretching is influenced by the same considerations as the x-ray diffraction, since it is observed only above a certain critical elongation and is greater the higher the elongation, the lower the temperature, and the longer the time the sample is kept stretched. The volume of stretched rubber is also affected by the composition and is particularly sensitive to the presence of coarse fillers and other inhomogeneities which give rise to vacuoles on stretching.

In the present investigation the influence of these different factors has been covered in an exploratory manner. The data which have been obtained are not sufficiently well coördinated or complete to permit the construction of any comprehensive polydimensional chart giving the volume of stretched rubber under any specified set of conditions.

Some consideration has been given to the probable effect of pressure on the volume of stretched rubber, but no data have been obtained.

Composition

As indicated previously, most of the work here described was done with two "pure-gum" compounds, but some measurements were made on compounds containing 10 per cent by volume of whiting and of carbon black, respectively, which illustrate two contrasting types of behavior. When the samples containing whiting were stretched, there was an increase in volume, which was greater the higher the elongation. But when these samples were held in the stretched condition the volume decreased with time, indicating that two effects were operating in different directions. During the stretching the rubber phase evidently pulled away from the filler particles and formed vacuoles of such magnitude as to cause a distinct increase in the volume of the sample as a whole, and to mask the decrease resulting from the fibering of the rubber phase. But when the sample was held in the stretched condition, the fibering continued and caused a distinct decrease in the volume of the sample with time, as may be seen in Fig. 4. On releasing the sample the volume returned almost but not quite to the original volume, the slight increment no doubt resulting from the presence of small amounts of gas, which prevented the complete collapse of the vacuoles.

When the compound containing 10 per cent of carbon black was stretched, there was a decrease rather than an increase in volume, as is illustrated by the results shown in Fig. 5. This decrease became apparent at an elongation of 190 per cent; this is somewhat lower than the elongation at which a decrease was observed with pure-gum rubber, a circumstance which is readily explained by the fact that the rubber phase in a compound containing filler is under greater actual elongation than that indicated by the stretch of the sample as a whole. The fact that there was no increase in volume with the sample containing carbon black is an indication that

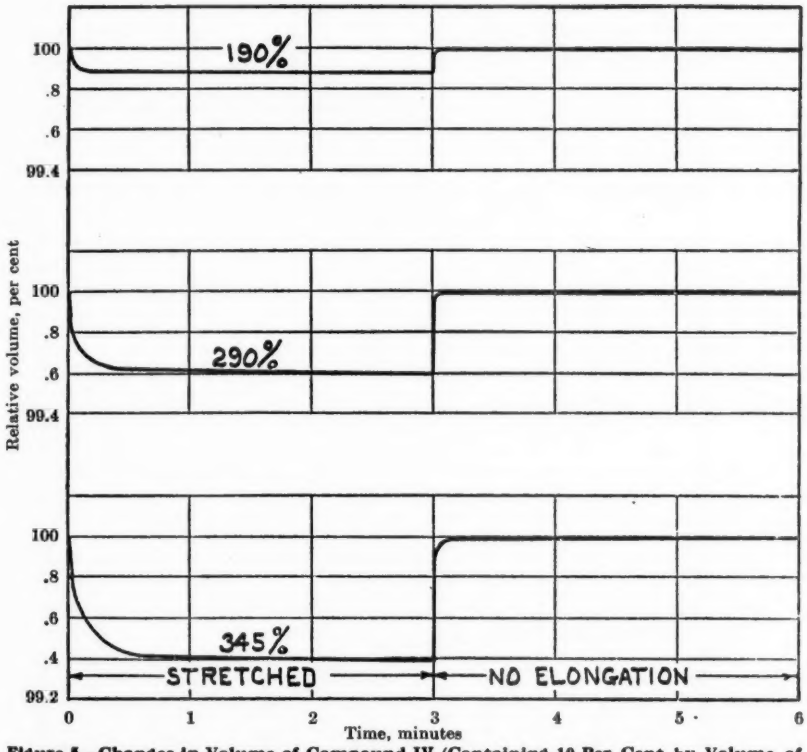

Figure 5—Changes in Volume of Compound IV (Containing 10 Per Cent by Volume of Carbon Black) when Stretched and when Released

the carbon black was present in such a state that no vacuoles were formed on stretching.

The relative behavior of the samples containing whiting and carbon black, respectively, suggests that the measurement of the change of volume on stretching may constitute a very simple and practical way of finding the nature and degree of dispersion of the filler in an unknown rubber compound.

Elongation[12]

Two series of experiments were conducted with samples made from compound *II* to ascertain the effect of elongation on the change of volume during the first few minutes after stretching. In one series, the rubber was stretched to a given elonga-

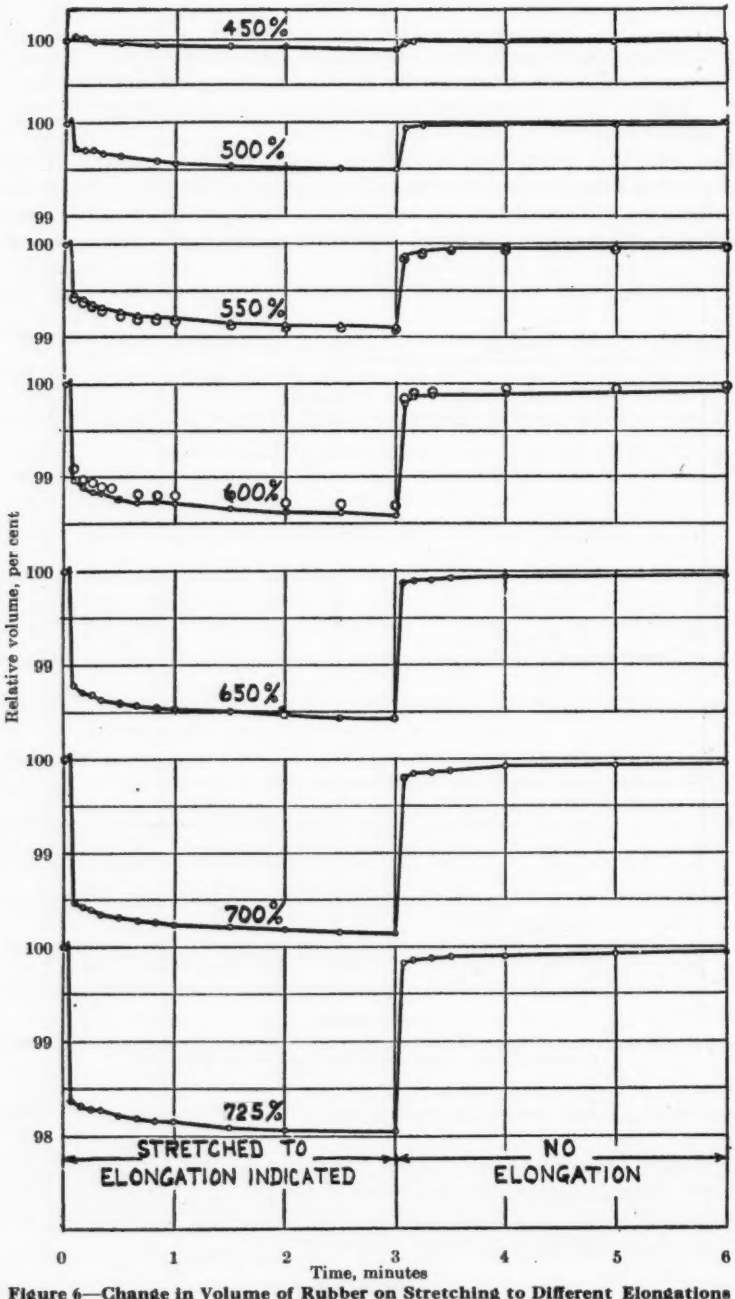

Figure 6—Change in Volume of Rubber on Stretching to Different Elongations at 25° C.

All tests were made on the same specimen which was stretched to the elongation indicated and held for 3 minutes, after which it was released and allowed to stand for 3 minutes before stretching to another elongation. The tests were made in the following order: —450 per cent elongation, 500, 550, 600, 550 (second test), 600 (second test), 650, 700, and 725. The results of the second tests are indicated by the large circles.

tion and held at that elongation for 3 minutes, observations on the volume being made at frequent intervals. It was then released and observations again taken at intervals over a period of 3 minutes. The same procedure was repeated for successive different elongations.

In a second series of experiments the samples were stretched first to a relatively low elongation, 200 per cent, and were held at this elongation for 3 minutes while observations were being made. Then, without release, the sample was stretched to successive higher elongations, each for 3 minutes, until the maximum elongation had been reached. The process was then reversed by the same stepwise procedure.

The results of the first series of experiments are shown graphically in Fig. 6. At an elongation of 450 per cent, the volume decreased by about 0.1 per cent in 3 minutes. At higher elongations the decrease became progressively greater, and amounted to nearly 2 per cent at an elongation of 725 per cent. After the observations had been made at elongations up to 600 per cent, a second set of readings was made on the same sample at elongations of 550 and 600 per cent, respectively. The results, which are indicated by large circles on the graph, are in practical agreement with the first set of observations. This, and other experiments of a similar character, indicated that the change of volume on stretching was not significantly affected by the previous stress history of the sample, provided that it had been allowed to retract completely from the previous stretching. This is in contrast to the stress-strain behavior which is markedly altered by the first few cycles of stressing.[13]

The results of the second series of experiments in which the samples were stretched by a stepwise procedure are shown in Fig. 7. The changes of volume at the different elongations were in general slightly greater than the changes which were observed when the samples were released between each two elongations.

When the sample was released in a stepwise manner the volume showed a decided lag, and at any elongation except zero it was less than the volume attained on stretching to the same elongation. At zero elongation, however, the original volume was resumed. It might be thought that the volume attained at any given elongation in the release cycle would represent the equilibrium or final value which would be attained if rubber were stretched initially to that elongation and held for a very long time. Experiments reported in a subsequent part of this paper, however, indicate that when rubber is held for a long time in the stretched condition the volume may reach lower values than those shown in Fig. 7, and still give no indication of having become constant.

After the sample which had been put through the stepwise cycle was released, it was stretched directly to 600 per cent elongation, at which it assumed a volume practically identical with that observed on stepwise stretching to the same elongation.

Time

The change of volume of stretched rubber with time is of such basic significance that it has, of necessity, been considered simultaneously with each of the other factors studied. Some observations, however, were made over relatively long periods in order to determine the nature of the relation between volume and time, and to ascertain whether a constant state would be reached. In these experiments mercury-filled dilatometers were employed in conjunction with dilatometers filled with water, and the curves obtained with the two instruments were joined at a point 20 minutes after stretching, as was indicated in a previous section. The results of two experiments are shown by the curves in Fig. 8. One curve represents the change of volume of a sample held at 550 per cent elongation for about 2 weeks at 0° C., and

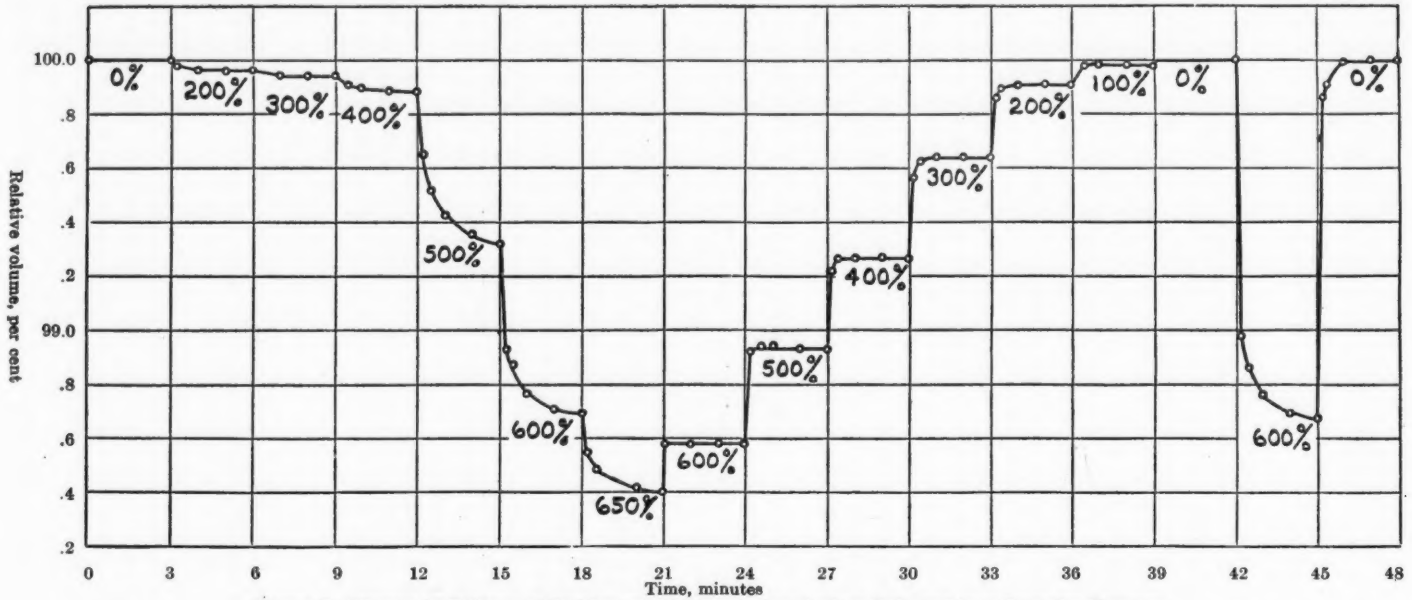

Figure 7—Change in Volume of Rubber when Stretched and when Released in a Stepwise Manner

All tests were made on the same sample which was successively stretched (or released) and held at each of the elongations indicated for 3 minutes

the other is for a similar sample held at 600 per cent elongation for over 3 weeks at 25° C.

The change of volume from minute to minute, or from day to day, rapidly became

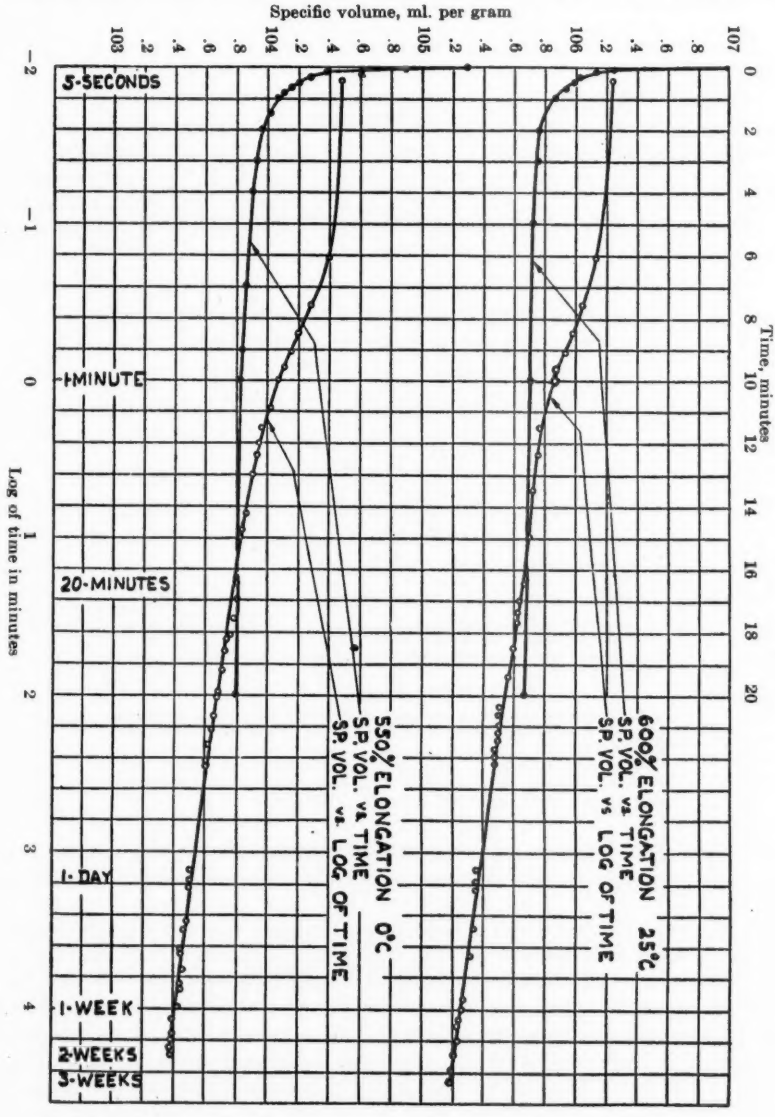

Figure 8—Change in Volume of Stretched Rubber over Long Periods of Time

less as time went on, but the volume did not become constant. When the volume was plotted against the logarithm of the time, the curves so obtained were approximately linear after the first few minutes, indicating that the change in the rubber

was proceeding at a constant rate with respect to the *logarithm of the time*. There was no indication that any limiting volume was being approached. It appears that observations over a considerably longer period of time will be required to give any definite indication of the final or equilibrium volume of stretched rubber. The inflection of the logarithmic curve at one minute is of course a natural characteristic of the curve, and does not indicate any discontinuity in the behavior of the rubber at that point.

Temperature

The effect of temperature on the change of volume was investigated at two intervals of time after stretching—one minute and several days. The former measurements were made by stretching samples of rubber in a water-filled dilatometer at different temperatures, and noting the volume change at the end of one minute.

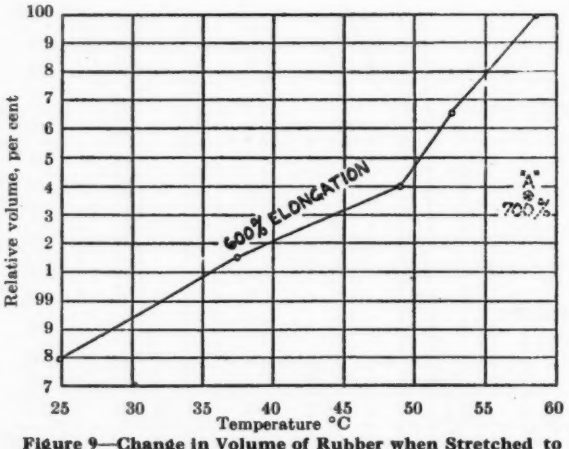

Figure 9—Change in Volume of Rubber when Stretched to 600 Per Cent Elongation and Held for 3 Minutes at Different Temperatures

The same sample of compound *I* was used in all tests. After stretching to 600 per cent at 58° C it was released and stretched to 700 per cent with the result indicated by point *A*

In the latter measurements a mercury-filled dilatometer containing a given sample was subjected to a series of temperatures, and the change of volume with temperature noted.

The results of the first series of experiments indicate that for a given elongation the change of volume becomes less the higher the temperature, a point ultimately being reached at which there is no change of volume on stretching. Typical results are shown in Fig. 9. At an elongation of 600 per cent, the change of volume ranges from 1.2 per cent at 25° C. to zero at 58° C. But when the same sample was stretched to 700 per cent at 58° C., there was a decrease in volume amounting to about 0.6 per cent. The curve shown in Fig. 9 is simply a broken line connecting the observed points. The present data do not warrant any assumption as to the precise nature of the function.

In the second series of experiments a sample was stretched to 600 per cent elongation at 25° C. in a dilatometer, with mercury as the confining liquid. A similar sample was mounted in another mercury-filled dilatometer of the same content as the first. After several days, when the decrease in the volume of the stretched

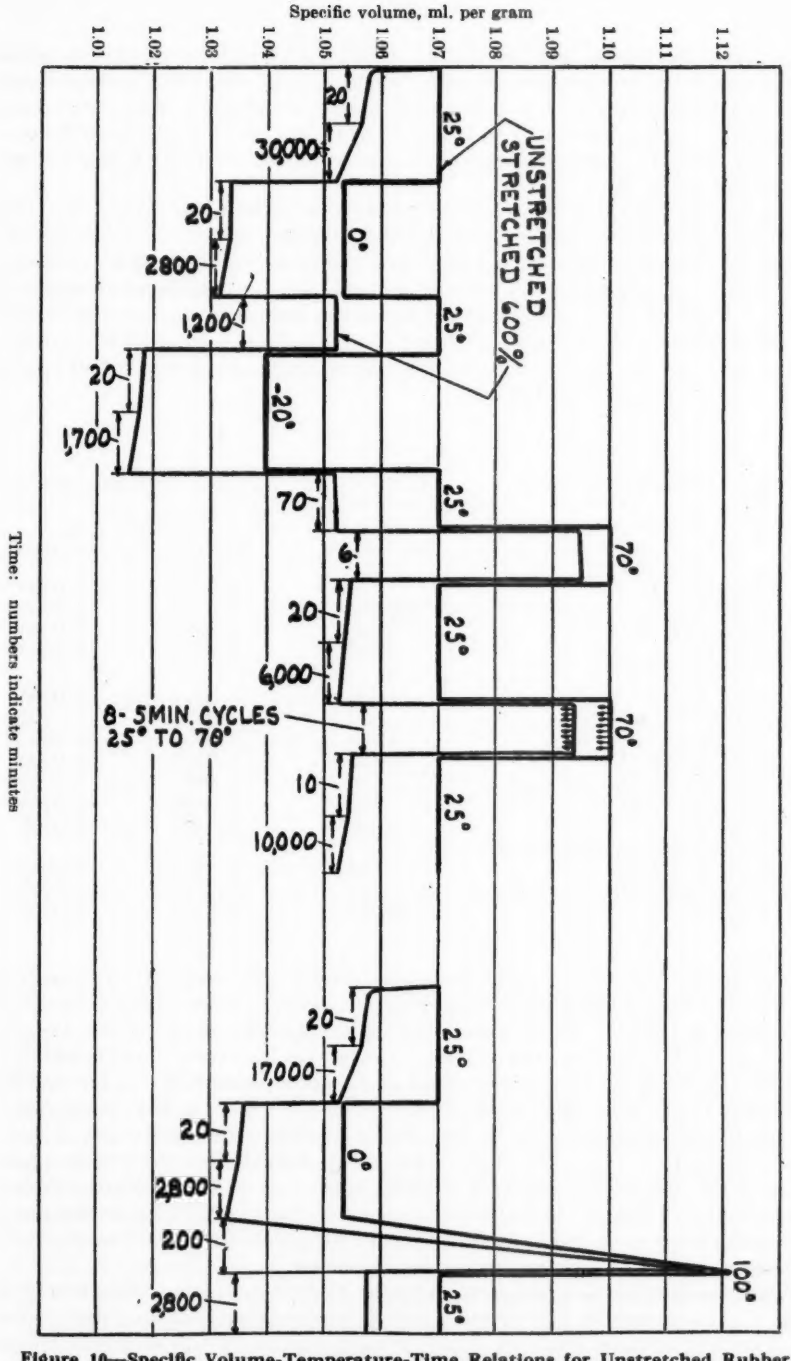

Figure 10—Specific Volume-Temperature-Time Relations for Unstretched Rubber and Rubber Stretched to 600 Per Cent Elongation

The two series of tests shown were conducted with two different samples of compound I

rubber from day to day had become very small, the two dilatometers were carried through cycles of temperature between 25 and 0, −20, and 70° C., respectively. Duplicate samples of rubber were then taken and further observations were made, this time at temperatures of 25, 0, 100, and 25° C., respectively. The results computed in terms of specific volume are summarized in Table II, and are shown graphically in Fig. 10.

The specific volume of the stretched rubber was, at all temperatures, less than that of the unstretched rubber. It was anticipated that at 70° C. the two samples would have the same specific volume, since the rubber underwent no change in volume when stretched to 600 per cent elongation at temperatures above about 58° C. However, such was found not to be the case, and even at 100° C. the stretched rubber had somewhat the lower specific volume. In order to show this aspect of the results more clearly, the specific volumes have been plotted against the temperature, as shown in Fig. 11.

TABLE II

EFFECT OF TEMPERATURE CYCLES ON THE SPECIFIC VOLUMES OF STRETCHED AND UNSTRETCHED RUBBER

Operation	Time Interval, Minutes	Specific Volume	
		Stretched 600%	Unstretched
Stretched at 25° C.	20	1.0567	1.0700
Held at 25° C.	30,000	1.0519	1.0700
Transferred to 0° C.	20	1.0329	1.0530
Held at 0° C.	2,800	1.0314	1.0530
Transferred to 25° C.	.....	.....	.....
Held at 25° C.	1,200	1.0519	1.0700
Transferred to −20° C.	20	1.0179	1.0405
Held at −20° C.	1,700	1.0158	1.0405
Transferred to 25° C.	70	1.0519	1.0700
Transferred to 70° C.	6	1.0949	1.1035
Transferred to 25° C.	20	1.0536	1.0700
Held at 25° C.	6,000	1.0526	1.0700
Transferred to 70° C. after 8 cycles at 25° to 70° C.	40	1.0935	1.1035
Transferred to 25° C.	10	1.0542	1.0700
Held at 25° C.	10,000	1.0521	1.0700

The curves for the stretched and the unstretched rubber, respectively, constitute two straight lines of different slopes which approach each other, but lack somewhat of meeting at 100° C. The points indicating the specific volume of the stretched rubber at the different temperatures scatter somewhat because of changes with time and with the thermal history of the sample. The lower point at 25° C., for example, represents the volume after 30,000 minutes (about 3 weeks) at that temperature; the upper point represents the volume after a number of cycles, the last of which was from 70° to 25° C. The slopes of the curves indicate that the volume expansivity of the unstretched rubber is 0.00067, while that of the stretched rubber is approximately 0.00083. It should be emphasized that the latter figure pertains to pure-gum rubber stretched to an elongation of 600 per cent for 2 to 4 weeks, and is in no sense a constant for stretched rubber in general.

When the sample which had been held at 25° C. for 3 weeks was cooled to 0° or to −20° C., it decreased in volume quite perceptibly on being kept for a day or so at the lower temperature, but when it was brought back to 25° C. the specific volume in each instance was the same as it had been before cooling. This indicates that at

least under some circumstances no advantage can be taken of thermal cycles to hasten the attainment of the equilibrium volume of stretched vulcanized rubber.

After the cycles between 25° C. and lower temperatures, the same sample was put through first one cycle, and then eight successive cycles between 25 and 70° C. The resultant effect was a small increase in the specific volume of the sample at 25° C.

State of Vulcanization

In order to determine whether the change of volume on stretching was affected by the state of vulcanization, measurements were made on samples of compound *I*, which had been vulcanized for different periods ranging from 15 to 60 minutes.

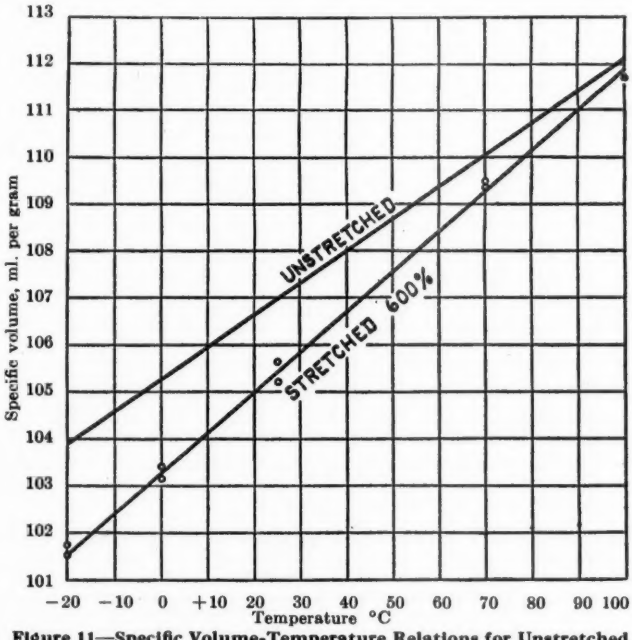

Figure 11—Specific Volume-Temperature Relations for Unstretched Rubber and Rubber Stretched to 600 Per Cent Elongation

Based on data from figure 10

At the shortest time the rubber was decidedly undercured, and at the longest it was overcured. The change of volume 1 minute after stretching was determined for each sample at a series of elongations, with results which are shown in Fig. 12. For any given sample the volume, above a certain critical elongation, was found to decrease in an approximately linear manner with increasing elongation. The curves for the different samples lie rather close together, and are roughly parallel, except that the curve for the sample having the 15-minute cure crosses some of the others. In general an increase in the time of vulcanization results in a decrease in the volume change at a given elongation. Also an increase in the time of vulcanization results in an increase in the elongation at which the change of volume first becomes apparent. The relative effect of the degree of vulcanization is likely to be much greater at low elongations than at high.

Other Factors

The results which were obtained in the course of this work did not show as high an order of precision as the methods and apparatus were capable of giving. Variations were encountered between different lots of samples which were prepared at intervals over a period of 2 years. For instance, when different samples of compound *I* were stretched to 600 per cent elongation at 25° C., the decreases in volume observed ranged from 1.1 to 1.5 per cent, with most of the values in the neighborhood of 1.2 per cent. This variation is probably due, in part at least, to bloom and inhomogeneities in the rubber, which would tend to cause an increase in volume on stretching. Some very erratic results which were obtained in the case of a compound vulcanized with 3 per cent of tetramethylthiuram disulfide were traced by microscopic examination to particles of the accelerator which had crystallized out

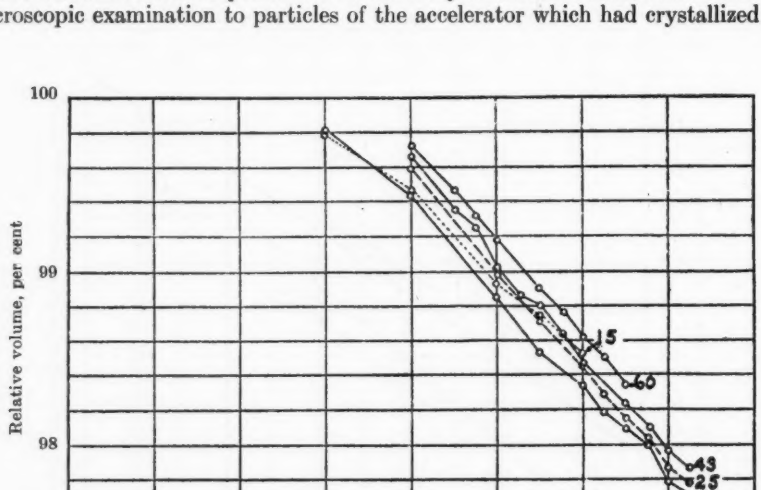

Figure 12—Effect of Time of Vulcanization on the Change in Volume of Rubber when Stretched to Different Elongations

Samples of compound *I* were vulcanized at 141° C for periods of from 15 to 60 minutes, as indicated on the curves. The change in volume was measured one minute after stretching

from the rubber. Inasmuch as the present investigation was exploratory in character, no critical study was made of the variations between different samples or different lots of rubber compound.

POISSON'S RATIO

Poisson's ratio for homogeneous rubber is precisely 0.5 at low elongations where there is no change of volume on stretching, and is greater than 0.5 at high elongations where the volume decreases on stretching. Inasmuch as this change in volume is dependent on the composition, the elongation, the temperature, and the time the sample is kept stretched, all of these factors must be specified in order to give significance to any numerical value for the ratio. Most of the values for Poisson's ratio which are given in the literature are less than 0.5 since they refer to rubber-

filler systems which increase in volume on stretching because of the formation of voids around the particles of filler.

Poisson's ratio has been defined for rubber by Vogt and Evans[14] as "the ratio of the percentage of lateral shrinkage of a rod to the corresponding percentage longitudinal increase, when such increase is infinitesimally small."

This may be expressed as,

$$P = -\frac{dS/S}{dL/L} \tag{1}$$

where S is the lateral dimension of the sample at any instant, L is the length at the same instant, and dS and dL are the corresponding infinitesimal changes in the two dimensions.

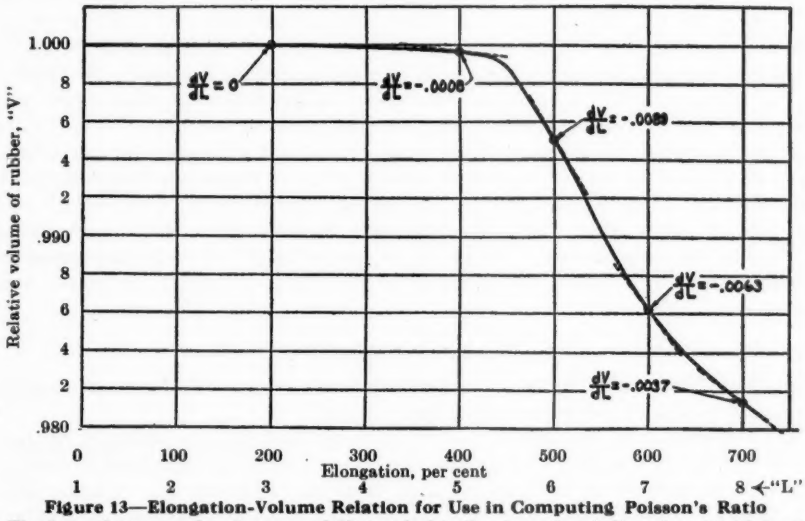

Figure 13—Elongation-Volume Relation for Use in Computing Poisson's Ratio
The data refer to samples of compound *II* stretched to the elongations indicated and held for 3 minutes at 25° C.

This definition may be expressed on a volume basis as,

$$P = 1/2 - 1/2\left(\frac{LdV}{VdL}\right) \tag{2}$$

where the initial volume is taken as unity and V is the volume at any instant.[15]

For purposes of illustration, Poisson's ratio has been computed from data shown in Fig. 6. The relative volumes 3 minutes after stretching have been taken from the different curves shown in this figure, and have been plotted against the elongation to give the curve shown in Fig. 13. The slope of this curve is dV/dL. The numerical values of the slope have been found at several points, as indicated on the graph, and have been used for the computation of the values of Poisson's ratio which are given in Table III. The slope is 0 up to 300 per cent elongation, making the ratio 0.500 for this range. Between 400 and 500 per cent elongation the slope increases rapidly, and at the latter elongation the ratio reaches its maximum value of 0.527; at higher elongations it decreases somewhat and drops to 0.515 at 700 per cent.

TABLE III

POISSON'S RATIO FOR COMPOUND *II* STRETCHED FOR 3 MINUTES AT 25° C.

Elongation Per Cent	Length L	Volume V	dV/dL	Poisson's Ratio
100	2	1.000	0.	0.500
200	3	1.000	0.	0.500
300	4	1.000	0.	0.500
400	5	0.9996	−0.0008	0.502
500	6	0.995	−0.0089	0.527
600	7	0.986	−0.0063	0.522
700	8	0.9815	−0.0037	0.515

INTERPRETATION OF RESULTS

Measurements of the volume changes associated with the stretching of rubber afford a simple quantitative means of studying the fibering or crystallization which is the basis for the well-known contrast between the properties of unstretched and stretched rubber. The present investigation has been conducted from the standpoint of developing simple facts and relations and exploring the field. No attempt has as yet been made to coördinate the results of the volume measurements with theories of the molecular structure and the mechanism of stretching. One limitation of the present results from the standpoint of their utilization for purposes of basic theory is that none of the volume change measurements has been followed to any ultimate or equilibrium state. The change with time *on a logarithmic scale* proceeds at a rate which shows no significant diminution for the longest periods covered by the present work. There can, of course, be no full understanding of the process of fibering until the end product has been prepared and its properties measured.

VII. SUMMARY

1. Two dilatometers have been described which are suitable for measuring the change of volume of rubber on stretching.

2. The volume of pure gum rubber remains constant up to a critical elongation, above which it decreases. Coarse fillers and other inhomogeneities tend to increase the volume because of the formation of vacuoles on stretching. Carbon-black compounds, however, decrease in volume above a critical elongation, which is lower than for pure gum.

3. The decrease in volume of rubber on stretching is greater the higher the elongation, the lower the temperature, or the longer the time the rubber is kept stretched.

4. After the first few minutes the volume of stretched rubber decreases at an approximately uniform rate with the logarithm of the time. No final or equilibrium state was attained in periods up to 3 or 4 weeks.

5. Stretched rubber shows a greater coefficient of expansion than unstretched rubber.

6. Poisson's ratio for rubber in the absence of coarse fillers is 0.5 or greater, the numerical value being a function of the composition, the elongation, the temperature, and the time after stretching.

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[7] W. W. Vogt and R. D. Evans, "Poisson's Ratio and Related Properties for Compounded Rubber," *Ibid.*, **15**, 1015–1018 (1923).

[8] A summary of the early work is given by Whitby in "Plantation Rubber and the Testing of Rubber," p. 486–501 (Longmans, Green and Co., London, 1920).

[9] See footnote 5.

[10] When water is taken up by unstretched rubber the swelled rubber occupies almost, if not precisely, the same volume as the rubber and the water taken separately, but in the case of stretched rubber there appears to be an appreciable net loss of volume on swelling. The authors do not wish to report numerical data regarding this effect until further experiments have been conducted.

[11] This precise duplication was not necessary in the case of the two water-filled dilatometers because, with them, a very nearly constant temperature was maintained for each test, whereas in the present case the temperature was sometimes changed over a wide range in the course of a test.

[12] The term "elongation" is used throughout this paper to mean the amount of stretch. A sample stretched to twice its original length, for example, has an elongation of 100 per cent.

[13] W. L. Holt, "Behavior of Rubber under Repeated Stresses," *Ind. Eng. Chem.*, **23**, 1471–1475 (1931).

[14] W. W. Vogt and R. D. Evans, "Poisson's Ratio and Related Properties for Compounded Rubber," *Ibid.*, **15**, 1015–1018 (1923).

[15] Equation 2 can be obtained from Equation 1 as follows:

$$V = KLS^2, \text{ where } K \text{ is a constant} \tag{3}$$

Differentiating,

$$dV = 2KLSdS + KS^2dL \tag{4}$$

Dividing Equation 4 by Equation 3

$$dV/V = 2dS/S + dL/L \tag{5}$$

or

$$\frac{dV/V}{dL/L} = \frac{2dS/S}{dL/L} + 1 \tag{6}$$

Combining Equations 6 and 1,

$$P = 1/2 - 1/2\left(\frac{LdV}{VdL}\right)$$

[Translated for Rubber Chemistry and Technology from Kautschuk, Vol. 13, No. 2, pages 17–23, February, 1937.]

Isoprene and Rubber

Part 46.[1] Viscosity Measurements of Gel Solutions of Rubber and Hydrorubber

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I. RELATIONS BETWEEN VISCOSITY AND CONCENTRATION WITHIN THE RANGE OF SOL AND GEL SOLUTIONS

Rubber and hydrorubber belong to that group of colloids known as lyophylic colloids. They are characterized by the fact that their solutions are extraordinarily viscous, even at low concentrations, and follow neither the Einstein nor the Hagen-Poiseuille law. It was pointed out in previous works[2] that this abnormal behavior of rubber solutions, as well as of many other natural and synthetic high molecular substances, depends on the long, thread-like form of their macromolecules. All these compounds belong to that class known as linear colloids.[3] With these solutions the relationships between viscosity, particle size, and number of particles are far different from those of solutions containing spherical particles (spherocolloids), for which the Einstein law is valid.[3a] Of the many attempts which have been made to derive some law relating the viscosity and concentration of rubber solutions, the formulas of Arrhenius,[4] Bingham,[5] and Fikentscher and Mark[6] may be mentioned. It is difficult to derive any general relation, because the state of rubber solutions may vary considerably with the size of the molecules and the concentration. This point has not been sufficiently taken into account in deducing previous formulas. The following three states of solution are to be distinguished, but it is self-evident that there are intermediate states between these.

1. Sol Solutions

In sol solutions the fiber molecules have free motion, *i. e.*, they are so few in number that the molecules present are able to move freely without disturbing one another. The viscosity of a solution in which the sphere of action[7] of all the dissolved fiber molecules is equal to the volume of the solution is designated the *critical viscosity*. The critical viscosity[8] of benzene solutions of polyprenes and polypranes is approximately 0.7. In solutions having a specific viscosity higher than 0.7, the fiber molecules have lost their freedom of motion. A rubber solution with a specific viscosity of 0.14 corresponds approximately to a 20 per cent solution of a substance of low molecular weight. In this type of solution it can be assumed that the molecules have freedom of motion. When diluted, these solutions form sol solutions, and only in this range does the specific viscosity increase in proportion to the concentration. The range of concentration in which viscosity measurements can be carried out, and in which the above condition is fulfilled, is therefore very limited; η_{sp} lies between 0.05 and 0.14. If the specific viscosity of a solution drops below 0.05, the experimental errors become excessive; if it becomes greater than 0.14, or at the most 0.2, then movement of the dissolved fiber molecules is no longer completely unimpeded in these highly viscous solutions, so that a strict proportionality between viscosity and concentration is no longer to be expected. Within the sol solution range, the following relationship is valid[9]:

$$\frac{\eta_{sp}}{C_{gm}} = K_m M \qquad (1)$$

The range of concentration of sol solutions is very different for low and high molecular compounds, as shown by the limiting concentrations of a few rubbers of differing degrees of polymerization. On the other hand the critical viscosities at these various limiting concentrations are always the same, *viz.*, $\eta_{sp} = 0.7$.

TABLE I

CRITICAL CONCENTRATION OF VARIOUS HOMOLOGOUS POLYMERIC RUBBERS

Substance	Average Molecular Weight	Average Degree of Polymerization	Critical Concentration (Change from Sol Solution to Gel Solution) C_{gm}	$\%\ C$
Raw Hevea rubber	170,000	2500	0.014	0.095
Rubber purified by the method of Pummerer (difficultly soluble)	68,000	1000	0.035	0.24
Masticated rubber	27,000	400	0.091	0.62
Hemicolloidal polyprene	6,800	100	0.35	2.4
Low molecular polyprene	680	10	3.5	24

2. Gel Solutions

If the limiting concentration is exceeded, *i. e.*, the concentration of solutions of high polymeric substances corresponding to their critical viscosities, gel solutions are formed. In this case only solutions of homopolar substances in homopolar solvents[10] are included. Such a state of solution is unknown in solutions of low molecular substances in homopolar solvents, and also in solutions of high molecular substances having spherical shaped particles. On the contrary, this is the characteristic state of solution in highly viscous solutions of high polymeric substances with linear shaped particles. This state of solution is characterized by the fact that the dissolved fiber molecules are completely solvated, though they no longer possess freedom of motion because of their wide sphere of action. An example of a gel solution is a 1 per cent solution of a eucolloidal rubber having a degree of polymerization of 2000, which corresponds to a specific viscosity of about 60. On the other hand, a 1 per cent solution of a hemicolloidal rubber having a degree of polymerization of 100 is a sol solution with a specific viscosity of 0.4. The gel solution of eucolloidal rubber is therefore about 150 times more viscous than a sol solution of hemicolloidal rubber at the same concentration.

Frequently the high viscosities of solutions of eucolloidal rubber are to be attributed to associations, or to the formation of micelles by the fiber molecules. This view is held even today by McBain.[11] On the basis of present knowledge, however, it can be assumed that the state of solvation of hemicolloidal and eucolloidal substances is the same in solutions of like concentration, because the number of isoprene residues which are solvated by the same quantity of solvent is the same in both cases. Therefore in highly viscous 1 per cent solutions of hemicolloidal rubber, just as little association is present as in solutions of hemicolloidal rubber of the same concentration but of low viscosity. In favor of the fact that the states of solvation of solutions of hemi- and eucolloidal substances of the same concentration but of widely differing viscosities are the same is the observation that, on heating from 20° to 60° C., the viscosity of solutions of the same concentration diminishes to the same extent. The influence of temperature on solutions of like concentration is therefore approximately the same,[12] in spite of the difference in the specific viscosities.

TABLE II

INFLUENCE OF TEMPERATURE ON THE SPECIFIC VISCOSITY OF TWO SAMPLES OF BALATA IN TETRALIN SOLUTIONS OF DIFFERENT CONCENTRATIONS

	Hemicolloidal Balata			Eucolloidal Balata		
C_{gm}	η_{sp} 20°	η_{sp} 60°	% Difference	η_{sp} 20°	η_{sp} 60°	% Difference
0.025	...	...	...	0.33	0.33	0
0.050	...	...	...	0.75	0.71	5.4
0.063	0.15	0.14	6.7	...	...	...
0.100	...	...	...	1.78	1.62	9.0
0.125	0.31	0.28	9.7	...	...	...
0.200	...	...	...	5.75	5.16	10.0
0.250	0.69	0.60	13.0	...	...	...
0.300	...	...	...	10.08	8.85	12.0
0.500	1.66	1.43	14.0	52.7	42.6	19.0
1.000	4.61	3.76	18.0	...	...	...

TABLE III

DETERMINATION OF THE CONCENTRATION CONSTANTS FOR HYDRORUBBER NO. 1, WITH AN AVERAGE MOLECULAR WEIGHT OF 25,000

$[\log(\eta_{sp}/C_{gm})]C \rightarrow 0$	C_{gm}	% C	η_{sp}	η_{sp}/C_{gm}	$\log(\eta_{sp}/C_{gm})$	K_{st}
In tetralin 0.87	0.1921	1.345	2.952	15.35	1.186	1.65
	0.2800	1.960	6.030	21.50	1.333	1.65
	0.2883	2.018	6.446	22.36	1.349	1.64
	0.2891	2.024	6.387	22.09	1.344	1.63
	0.4200	2.940	15.530	37.00	1.568	1.66
	0.4340	3.038	16.700	38.48	1.585	1.64
	0.5600	3.920	34.800	62.20	1.793	1.65
	0.5764	4.035	35.918	62.31	1.795	1.60
In carbon tetrachloride 1.00	0.1380	0.966	2.24	16.20	1.211	1.52
	0.1422	0.9954	2.34	16.46	1.217	1.52
	0.2070	1.449	4.46	21.60	1.333	1.61
	0.2143	1.500	4.53	21.16	1.325	1.52
	0.2760	1.932	7.60	27.50	1.440	1.59
	0.2875	2.015	7.90	27.51	1.440	1.54
	0.5910	4.130	47.70	80.80	1.907	1.53
In benzene 0.72	0.1447	1.013	1.384	9.500	0.983	1.81
	0.1443	1.010	1.370	9.495	0.978	1.78
	0.2140	1.498	2.614	12.210	1.087	1.71
	0.2880	2.016	4.671	16.220	1.210	1.75
	0.3720	2.605	9.800	26.350	1.421	1.87
	0.6200	4.343	44.000	71.000	1.851	1.82
In cyclohexane 1.06	0.0714	0.500	1.014	14.14	1.150	1.26
	0.1447	1.013	2.625	18.14	1.259	1.38
	0.2146	1.502	4.856	22.63	1.355	1.38
	0.2867	2.007	8.154	28.44	1.454	1.38
	0.3567	2.497	13.120	36.87	1.567	1.42
	0.4333	3.033	19.970	46.09	1.664	1.40

The high viscosities of gel solutions is solely the result of mutual interference of the long solvated fiber molecules when the limiting concentrations are exceeded. Since this mutual interference increases extraordinarily rapidly with increase in concentration, the specific viscosity in this range can no longer be expected to increase in proportion to the concentration. The viscosity increases much more rapidly, in fact it follows the law shown below:

$$\frac{\eta_{sp}}{C_{gm}} = K_m M e^{CK_{st}} \qquad (2a)$$

It has already been pointed out in connection with solutions of polystyrenes[13] that the following relationship between specific viscosity and concentration holds true:

$$\log\left(\frac{\eta_{sp}}{C_{gm}}\right) = K_{st}C + \log\left(\frac{\eta_{sp}}{C_{gm}}\right) C \longrightarrow 0 \qquad (2b)$$

Here K_{st} is a concentration constant which is characteristic of every polystyrene, and which has approximately the same value in different solvents. The concentration constant of polystyrenes of various molecular weights has different values; in fact it increases in proportion to the chain length, so that the following relationship also holds true:

$$K_{st} = MK_{mst} + b \qquad (3)$$

In this formula K_{mst} is another constant, the molecular weight-concentration constant. In order to determine this constant, the molecular weight M in a coordinate system is plotted as abscissa, and the concentration constant K_{st} as ordinate. The intersection b on the ordinate is then determined by extrapolation. With the aid of Equation 3, the molecular weight of polystyrenes can be estimated by means of viscosity measurements in the gel solution range. It will be shown by the following experiments that the same relationships (Equations 2 and 3) are valid for gel solutions of rubber and hydrorubber as well.

TABLE IV

DETERMINATION OF THE CONCENTRATION CONSTANT OF HYDRORUBBER RUBBER NO. 2, WITH AN AVERAGE MOLECULAR WEIGHT OF 14,000

$[\log(\eta_{sp}/C_{gm})]\ C \rightarrow 0$	C_{gm}	%C	η_{sp}	η_{sp}/C_{gm}	$\log(\eta_{sp}/C_{gm})$	K_{st}
In tetralin 0.71	0.1485	1.040	1.002	6.750	0.829	0.80
	0.1980	1.386	1.426	7.206	0.858	0.75
	0.2316	1.621	1.768	7.635	0.883	0.75
	0.2970	2.079	2.475	8.335	0.921	0.72
	0.5938	4.157	8.938	15.050	1.178	0.79
In carbon tetrachloride 0.76	0.1437	1.006	1.109	7.717	0.887	0.89
	0.2200	1.5400	1.986	9.027	0.956	0.89
	0.2857	2.000	2.957	10.350	1.015	0.89
	0.3670	2.572	4.830	13.180	1.119	0.98
In benzene 0.57	0.2147	1.503	1.149	5.351	0.728	0.74
	0.2967	2.077	1.835	6.185	0.791	0.75
	0.3800	2.660	2.948	7.758	0.890	0.84
	0.5286	3.700	5.164	9.786	0.990	0.78
In cyclohexane 0.79	0.1443	1.010	1.190	8.240	0.916	0.87
	0.2180	1.526	2.062	9.459	0.976	0.84
	0.2868	2.008	3.045	10.620	1.026	0.82
	0.3580	2.506	4.425	12.360	1.092	0.83
	0.4300	3.010	5.913	13.750	1.138	0.81

3. Associations

If the quantity of solvent is not sufficient to solvate completely each individual molecule of the dissolved substance, association takes place in solutions of homopolar substances in homopolar solvents.[14] In an earlier publication[15] it was shown that the solution of a homopolar substance in a solvent can be regarded as a van der Waals compound of dissimilar molecules. On the contrary, a pure compound

and a pure solvent represent van der Waals compounds of molecules of the same kind. If the concentration of the dissolved substance in the solution is very high, there are insufficient molecules in the solvent to solvate completely the dissolved molecules. As a result, van der Waals compounds between the dissolved molecules are formed, *i. e.*, associations are formed. The tendency to form such associations naturally depends both on the nature of the dissolved substance and on that of the solvent. Nevertheless it may be assumed that in a 1 per cent solution the dissolved molecules are completely solvated, independent of their size, provided that a good solvent is present. Associations are evident for the first time when the concentration of the solution is 10 per cent or more. For instance, in a 20 per cent solution, the quantity of solvent is not sufficient to surround every individual molecule with a film of solvate, so in this case associations are formed. However, it is not possible to prepare such a solution of a eucolloidal rubber; for example, 20 grams of rubber and 80 grams of benzene form a greatly swollen but still solid jelly. On the other hand, such highly concentrated solutions are obtained from a hemicolloidal, highly degraded rubber having a degree of polymerization of 100. The specific viscosity of such a solution is approximately 60, and is about the same as that of a 1 per cent solution of a eucolloidal rubber having a degree of polymerization of 200.0.

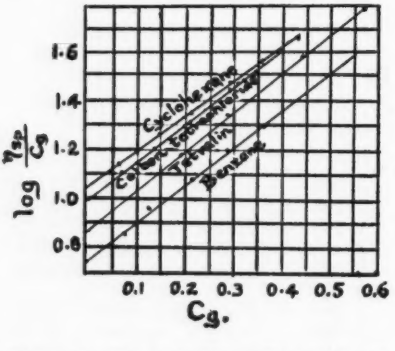

Figure 1—Concentration Constant of Hydro-rubber of M = 25,000 in Various Liquids

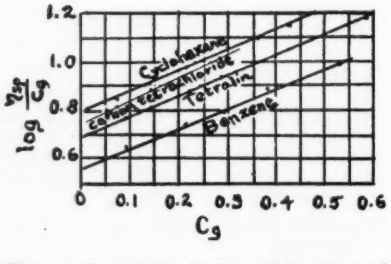

Figure 2—Concentration Constant of Hydro-rubber of M = 14,000 in Various Solvents

In spite of the similar viscosities of these solutions, the states of solution of the molecules are wholly different. The 1 per cent solution of eucolloidal rubber is a typical gel solution, the high viscosity of which depends on the mutual interference of the long fiber molecules. On the contrary, the viscosity of a 20 per cent solution of hemicolloidal rubber depends on the formation of colonies by association of the molecules. This can be shown by the fact that the specific viscosity of the gel solution is changed only slightly by warming. The viscosity of a highly concentrated solution of a hemicolloidal product depends to a large extent on the temperature, because the very loose associations are in this way more or less destroyed.[15a] The same relationship between viscosity and concentration cannot be expected of a highly viscous, very concentrated solution of a hemicolloidal rubber, as is to be expected of an equally viscous but less concentrated gel solution of eucolloidal rubber; for the relations between specific viscosity and concentration in the range within which associations occur are different and more complicated than in the range of pure gel solutions.

II. VISCOSITY MEASUREMENTS OF GEL SOLUTIONS OF HYDRORUBBER

Viscosity measurements in the range of gel solutions were carried out with three hydrorubbers[16] having average molecular weights[17] of 5000, 14,000, and 25,000, respectively. The concentrations of the solutions were so chosen that the specific viscosities lay in the range between 1 and 50,[18] and therefore exceeded the critical viscosity of approximately 0.7. In order to determine the influence of solvents on the value of the concentration constant, measurements were made in four different solvents, *viz.*, benzene, cyclohexane, tetralin, and carbon tetrachloride. The concentration constants found in these experiments for the three hydrorubbers are

TABLE V

DETERMINATION OF CONCENTRATION CONSTANT OF HYDRORUBBER NO. 4, WITH AN AVERAGE MOLECULAR WEIGHT OF 5000

$[\log(\eta_{sp}/C_{gm})]\ C \rightarrow 0$	C_{gm}	%C	η_{sp}	η_{sp}/C_{gm}	$\log(\eta_{sp}/C_{gm})$	K_{st}
In tetralin 0.28	0.3772	2.640	0.9471	2.511	0.400	0.31
	0.5788	4.052	1.663	2.874	0.548	0.31
	0.7544	5.281	2.463	3.265	0.514	0.31
	1.1580	8.106	5.037	4.351	0.639	0.31
In carbon tetrachloride 0.35	0.2900	2.030	0.820	2.828	0.451	0.35
	0.3560	2.492	1.068	3.000	0.477	0.36
	0.4393	3.075	1.397	3.180	0.502	0.35
	1.0860	7.608	6.330	5.830	0.766	0.38
In benzene 0.22	0.3791	2.654	0.809	2.134	0.329	0.29
	0.4498	3.149	1.014	2.254	0.353	0.30
	0.7447	5.213	2.157	2.896	0.462	0.33
	0.8940	6.258	2.892	3.235	0.509	0.33
	1.2120	8.484	4.778	3.942	0.596	0.31
In cyclohexane 0.38	0.3660	2.562	1.061	2.899	0.462	0.22
	0.3781	2.647	1.1700	3.094	0.491	0.29
	0.4447	3.113	1.446	3.251	0.512	0.29
	0.6194	4.336	2.261	3.650	0.562	0.29
	0.7580	5.306	3.054	4.029	0.605	0.29
	1.1540	8.078	6.317	5.473	0.738	0.31

TABLE VI

COMPARISON OF THE DEGREES OF POLYMERIZATION OF HYDRORUBBERS, OBTAINED BY CALCULATION FROM MEASUREMENTS IN SOL SOLUTIONS, WITH THE VALUES CALCULATED FROM THE LIMITING VALUES IN GEL SOLUTIONS

Molecular Weight	Solvent	$\eta_{sp}(1.4\%)$	Degree of Polymerization $\eta_{sp}(1.4\%) = n.y$	$[\log(\eta_{sp}/C_{gm})]$ $C \rightarrow 0$	Degree of Polymerization[18a] $\eta/_{sp}C_{gm} = K_m \cdot M$
25,000	CCl_4	2.12	313	1.00	314
	C_6H_{12}	2.44	358	1.06	352
	$C_{10}H_{12}$	1.85	355	0.87	321
	C_6H_6	1.21	232	0.72	250
14,000	CCl_4	1.25	184	0.76	180
	C_6H_{12}	1.35	199	0.79	189
	$C_{10}H_{12}$	1.09	210	0.71	222
	C_6H_6	0.73	140	0.57	177
5,000	CCl_4	0.48	71	0.35	70
	C_6H_{12}	0.47	69	0.38	73
	$C_{10}H_{12}$	0.44	85	0.28	83
	C_6H_6	0.38	73	0.22	79

summarized in Tables III, IV, and V. These results show that the K_{st} values for a definite solvent are constant within the limits of error.

The value for the lim $[\log(\eta_{sp}/C_{gm})]$ $C \rightarrow 0$ can be determined in two independent ways: (1) by measurements in sol solutions, in which case η_{sp}/C_{gm} is a constant, so that its logarithm represents the desired value, and (2) by graphic extrapolation of measurements in the range of gel solutions (see the graphs in Figs. 1, 2, and 3). Both methods should lead to the same limiting values. As is evident in Table VI, in general the values agree satisfactorily.

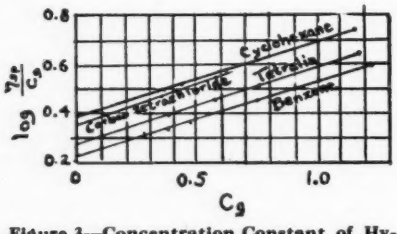

Figure 3—Concentration Constant of Hydrorubber of M = 5000 in Various Solvents

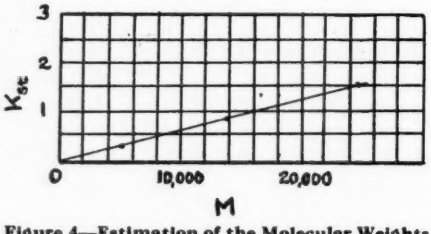

Figure 4—Estimation of the Molecular Weights of Hydrorubbers from Their Concentration Constants

In an earlier publication[19] it was assumed that the concentration constant K_{st} is independent of the solvent, and that deviations are attributable to experimental errors. The new results show, on the contrary, that both the concentration constant and the K_m constant vary somewhat with the nature of the solvent. However, the experimental results described do not give evidence of any close relationship between the solvation and the magnitude of this concentration constant.[19a]

The concentration constant of hydrorubbers increases in direct proportion to the molecular weight. Fig. 4 shows this relation.

If now the molecular weight of the hydrorubber under examination is calculated first from the results of viscosity measurements in gel solutions by Formulas 2*b* and 3, and secondly from measurements in the range of sol solutions by Formula 1, the two values obtained are in very good agreement, as is exemplified by the data in Table VII.

TABLE VII

COMPARISON OF THE MOLECULAR WEIGHTS OF HYDRORUBBER BY VISCOSITY MEASUREMENTS IN THE RANGE OF SOL AND GEL SOLUTIONS

$K_{mst} = 5.85 \times 10^{-5}$; $b = 0.07$; y in $CCl_4 = 1.7 \times 10^{-3}$

C_{gm}	%C	η_{sp}	η_{sp}(1.4%)	Molecular Weight in Sol Solution	K_{st}	Molecular Weight in Gel Solution
0.020	0.140	0.2199	2.199	25,000	1.53	25,000
0.028	0.193	0.1728	1.254	14,000	0.89	14,000
0.040	0.278	0.0936	0.480	5,000	0.35	5,000

It would have been desirable to extend these experiments to hydrorubbers of higher molecular weights, but adequate quantities were difficult to obtain.[20]

III. VISCOSITY MEASUREMENTS OF GEL SOLUTIONS OF MASTICATED RUBBER

A series of homologous polymers of mesocolloidal rubbers of various degrees of polymerization were prepared by mastication of eucolloidal rubber.[21] The molecu-

lar weights of these rubbers were determined first by viscosity measurements in the range of sol solutions. Viscosity measurements were then carried out in tetralin and carbon tetrachloride solutions of various concentrations, the specific viscosities of which varied from 1 to 50 (see Tables IX, X, and XI).

TABLE VIII

DETERMINATION OF THE CONCENTRATION CONSTANT OF MASTICATED RUBBER WITH A MOLECULAR WEIGHT OF 51,000

$[\log(\eta_{sp}/C_{gm})]\ C \to 0$	C_{gm}	$\%C$	η_{sp}	η_{sp}/C_{gm}	$\log(\eta_{sp}/C_{gm})$	K_{st}
In tetralin 1.370	0.074	0.504	2.37	32.0	1.505	1.83
	0.148	1.008	6.51	44.0	1.643	1.85
	0.222	1.512	13.25	59.7	1.776	1.83
	0.296	2.016	24.50	82.8	1.918	1.85
In carbon tetrachloride 1.490	0.075	0.509	3.50	46.7	1.669	2.39
	0.149	1.018	10.92	73.3	1.865	2.52
	0.224	1.527	24.70	110.0	2.043	2.46
	0.299	2.036	48.00	160.5	2.206	2.39

TABLE IX

DETERMINATION OF THE CONCENTRATION CONSTANT OF MASTICATED RUBBER NO. 1 WITH A MOLECULAR WEIGHT OF 31,000

$[\log(\eta_{sp}/C_{gm})]\ C \to 0$	C_{gm}	$\%C$	η_{sp}	η_{sp}/C_{gm}	$\log(\eta_{sp}/C_{gm})$	K_{st}
In tetralin 1.15	0.074	0.500	1.18	15.95	1.203	1.19
	0.147	1.000	3.07	20.90	1.320	1.39
	0.221	1.500	5.65	25.60	1.408	1.33
	0.294	2.000	9.42	32.00	1.505	1.33
	0.595	4.056	40.10	67.20	1.827	1.20
In carbon tetrachloride 1.28	0.074	0.500	1.74	23.50	1.371	1.22
	0.147	1.000	4.60	31.30	1.496	1.46
	0.221	1.500	8.62	39.00	1.591	1.40
	0.294	2.000	15.14	51.50	1.712	1.46

TABLE X

DETERMINATION OF THE CONCENTRATION CONSTANT OF MASTICATED RUBBER NO. 3 WITH A MOLECULAR WEIGHT OF 17,500

$[\log(\eta_{sp}/C_{gm})]\ C \to 0$	C_{gm}	$\%C$	η_{sp}	η_{sp}/C_{gm}	$\log(\eta_{sp}/C_{gm})$	K_{st}
In tetralin 0.945	0.1464	0.995	1.70	11.60	1.065	0.82
	0.2929	1.991	4.45	15.20	1.182	0.81
	0.4392	2.986	9.01	20.50	1.312	0.84
	0.5856	3.982	14.60	25.00	1.397	0.77
In carbon tetrachloride 1.065	0.1446	0.983	2.36	16.33	1.213	1.02
	0.2893	1.967	6.70	23.18	1.365	1.04
	0.4339	2.950	13.45	31.00	1.491	0.99
	0.5785	3.934	23.50	40.60	1.609	0.94

The $\lim[\log(\eta_{sp}/C_{gm})]\ c \to 0$ was also determined by graphical extrapolation. This value was necessary for determining the concentration constant. Here too it was not independent of the nature of the solvent, as was particularly true with the higher molecular rubbers; in fact in carbon tetrachloride, a good solvent which gives viscous solutions, the concentration constant was a higher value than in tetralin, which is a poorer solvent.[22]

The literature contains a large amount of data on viscosity measurements of solutions of homologous polymeric rubbers at various concentrations. From these

data we determined the concentration constants after determining the $\log(\eta_{sp}/C_{gm})$ $C \rightarrow 0$ values by graphical extrapolation (see Fig. 6 and Table XI).

TABLE XI

CALCULATION OF THE CONCENTRATION CONSTANT FROM EARLIER VISCOSITY MEASUREMENTS

Author	Solvent $\left[\log \frac{\eta_{sp}}{C_{gm}}\right]_{C \rightarrow 0}$	C_{gm}	η_{sp}	$\frac{\eta_{sp}}{C_{gm}}$	$\log \frac{\eta_{sp}}{C_{gm}}$	K_{st}	K_{st} (average)
Fikentscher and Mark[a]	C_6H_5Cl	0.0485	0.8	16.5	1.217	1.80	1.85
	1.13	0.0578	1.0	17.3	1.238	1.87	
	43,000	0.0790	1.5	19.0	1.279	1.90	
		0.0975	2.0	20.5	1.312	1.85	
Staudinger and Bondy[b]	C_6H_6	0.050	0.911	18.2	1.260	2.0	2.15
	1.16	0.100	2.430	24.3	1.386	2.3	
	48,000						
Staudinger and Bondy[b]	C_6H_6	0.050	1.442	28.9	1.461	2.82	2.58
	1.32	0.100	3.565	35.7	1.553	2.33	
	67,000						
Fikentscher and Mark[a]	C_6H_5Cl	0.0253	0.8	31.6	1.500	3.56	3.64
	1.41	0.0302	1.0	33.1	1.520	3.64	
	80,000	0.0412	1.5	36.4	1.561	3.64	
		0.0507	2.0	39.5	1.597	3.68	
Fol[c]	C_6H_6	0.0368	1.82	49.5	1.695	3.95	4.25
	1.55	0.0736	5.58	75.8	1.880	4.50	
	98,000	0.147	22.35	152.0	2.182	4.30	
Fol[c]	C_6H_6	0.368	1.97	53.5	1.728	4.30	4.84
	1.57	0.0736	6.46	87.7	1.943	5.03	
	102,000	0.1470	29.03	199.0	2.299	4.97	
		0.2206	102.37	465.0	2.667	4.99	
van Rossem[d]	C_6H_6	0.0884	14.5	164.0	2.214	6.84	6.71
	1.61	0.1030	19.7	192.0	2.283	6.51	
	130,000	0.128	38.5	301.0	2.479	6.80	
		0.147	58.5	400.0	2.602	6.74	
Staudinger[e]	C_6H_6	0.0125	0.68	54.4	1.736	6.1	6.90
	1.66	0.025	1.65	66.0	1.820	6.4	
	147,000	0.050	5.41	108.2	2.033	7.4	
		0.100	23.40	234.0	2.369	7.1	
		0.200	253.80	1269.0	3.103	7.2	

[a] *Kolloid-Z.*, **49**, 140 (1929).
[b] *Ber.*, **63**, 734 (1930).
[c] *Kolloid-Z.*, **12**, 143 (1913).
[d] *Kolloidchem. Beihefte*, **10**, 85 (1919).
[e] *Ber.*, **63**, 921 (1930).

The molecular weights of these rubbers were determined by Formula 1. In a few cases, where viscosity measurements were in the range of sol solutions, the η_{sp}/C_{gm} values could be obtained directly from this equation. In other cases, where the viscosity measurements had been carried out only in the range of gel solutions, the limiting value $[\log(\eta_{sp}/C_{gm})]$ $C \rightarrow 0$ was determined graphically, and the (η_{sp}/C_{gm}) value determined in this way. It was then possible, by means of Formula 1, to calculate the molecular weight and the degree of polymerization. With these homologous polymeric rubbers, the K_{st} constant increased in direct proportion to the increase in molecular weight, as is evident from Fig. 7. The dif-

ferences in the viscosity in the various solvents were disregarded in these calculations. The values of K_{mst} and b were then obtained, and when these values were introduced in Equation 3, the following equation was obtained. This new equation makes possible the calculation of the molecular weights of homologous polymeric rubbers from measurements of their viscosities in the range of gel solutions.

$$M = \frac{K_{st} + 0.2}{4.83 \times 10^{-5}} \tag{4}$$

The molecular weights of various homologous polymeric rubbers can thus be calculated in two ways, *viz.*, by this new Equation 4 and from the (η_{sp}/C_{gm}) values according to Equation 1. Approximately the same molecular weights are obtained by the two equations. In this way the molecular weight of rubber can be determined, not only in the range of sol solutions by means of viscosity measure-

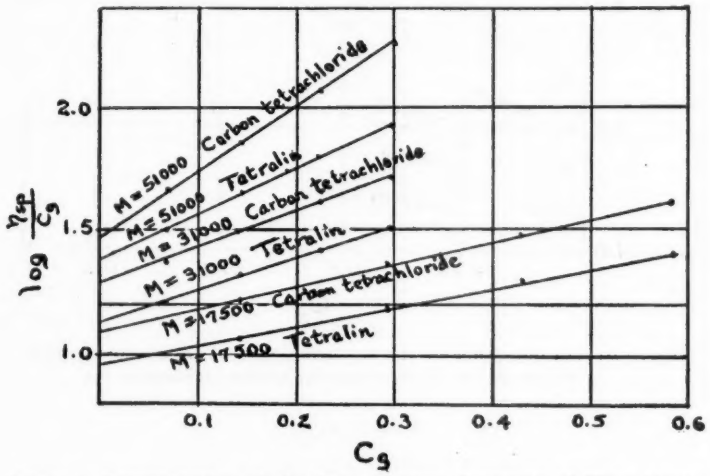

Figure 5—Determination of the Concentration Constants of Three Masticated Rubbers in Tetralin and in Carbon Tetrachloride

ments, but also in the range of gel solutions by means of Equation 4 (with the aid of a few viscosity measurements in the gel solution range in order to calculate the K_{st} constant).

The molecular weight concentration constant K_{mst} is characteristic of every homologous series of polymers. When it is determined for rubber, the viscosity of a rubber solution of any concentration can then be determined by means of Equation 4, in so far as its molecular weight is known, *e. g.*, by viscosity measurements in the sol solution range. In these calculations it is assumed that the viscosity measurements are carried out in the gel solution range, and not in highly concentrated solutions, in which association has taken place.

The K_{st} value of a rubber of definite molecular weight can either be calculated by Equation 4 or be derived very simply by the graphical method, shown in Fig. 7. When this K_{st} value is obtained, the specific viscosity of a particular rubber solution can be calculated by Equation 2, in which case it is convenient to convert the latter into the following form:

$$\log(\eta_{sp}/C_{gm}) = K_s C + \log(K_m M) \tag{5}$$

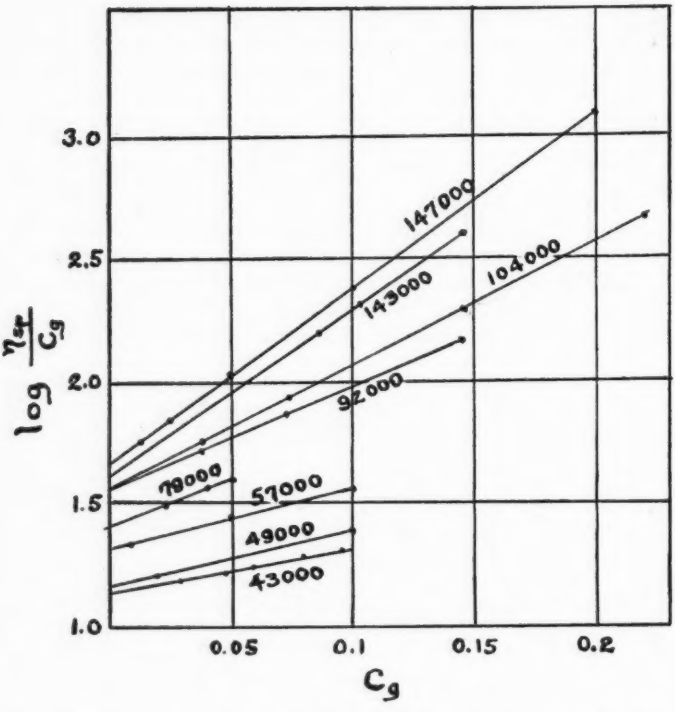

Figure 6—Determination of the K_{sf} Constant According to Viscosity Measurements Recorded in the Earlier Literature

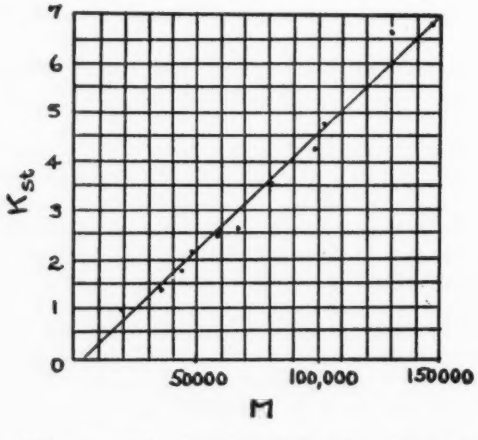

Figure 7—Determination of the K_m Constant from the Concentration Constants of Rubbers of Various Degrees of Polymerization

calculated in this way, the values of the specific viscosity of a rubber solution of definite concentration agree very well with those obtained experimentally. An actual example will serve to illustrate this. Calculated by Equation 5, the specific viscosity of a 1 per cent solution of rubber of molecular weight 150,000 was 90; the experimental value was 92. A 0.92 per cent solution of the same rubber gave a calculated specific viscosity of 68; an experimental value of 63.

In this way it becomes possible to calculate the specific viscosity of a concentrated rubber solution when its molecular weight-concentration constant is known.

TABLE XII

COMPARISON OF MOLECULAR WEIGHTS OF HOMOLOGOUS POLYMERIC RUBBERS CALCULATED FROM VISCOSITY MEASUREMENTS IN THE RANGE OF SOL SOLUTIONS ACCORDING TO FORMULA 1 WITH THOSE CALCULATED ACCORDING TO FORMULA 4

Author	Solvent	C_{gm}	η_{sp}	$\frac{\eta_{sp}}{C_{gm}}$	Molecular Weight by Formula 1	K_{st}	Molecular Weight by Formula 4
	$C_{10}H_{12}$	0.0132	0.087	6.49	17,500	0.81	21,000
	$C_{10}H_{12}$	0.0149	0.165	11.37	31,000	1.30	31,000
	$C_{10}H_{12}$	0.0072	0.136	18.95	51,000	1.84	42,000
Fikentscher and Mark[a]	C_6H_5Cl	0.0209	0.3	14.5	39,000	1.83	43,000
Staudinger and Bondy[b]	C_6H_6	0.01	0.157	15.7	43,600	2.15	49,000
Staudinger and Bondy[b]	C_6H_6	0.01	0.22	22.0	60,000	2.58	57,000
Fikentscher and Mark[a]	C_6H_5Cl	0.0113	0.3	26.5	72,000	3.60	79,000
Fol[c]	C_6H_6	0.0093	0.3	32.3	88,000	4.25	92,000
Fol[c]	C_6H_6	0.0089	0.3	33.8	92,000	4.84	104,000
van Rossem[d]	C_6H_6	0.007	0.3	43.0	116,000	6.71	143,000
Staudinger[e]	C_6H_6	0.0062	0.3	48.5	131,000	6.90	147,000

[a] *Kolloid-Z.*, **49**, 140 (1929).
[b] *Ber.*, **63**, 734 (1930).
[c] *Kolloid-Z.*, **12**, 143 (1913).
[d] *Kolloidchem. Beihefte*, **10**, 85 (1919).
[e] *Ber.*, **63**, 921 (1930).

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[1] For the 45th Communication see *Kautschuk*, **12**, 159 (1936); RUBBER CHEM. AND TECH. **9**, 579 (1936).

[2] Staudinger, "Die Hochmolekularen Organischen Verbindungen-Kautschuk und Cellulose," Berlin, **1932**; *Ibid.*, **6**, 153 (1930); **10**, 157, 170, 192 (1934).

[3] Staudinger, *Ber.*, **68**, 1682 (1935).

[3a] Bancelin, *Compt. rend.*, **152**, 1382 (1911); Staudinger and Husemann, *Ber.*, **68**, 1691 (1935).

[4] Arrhenius, *Biochem. J.*, **11**, 112 (1917).

[5] Bingham, "Fluidity and Plasticity," New York, **1922**.

[6] Fikentscher and Mark, *Kolloid-Z.*, **49**, 135 (1929).

[7] Staudinger, "Die Hochmolekularen Organischen Verbindungen-Kautschuk und Cellulose," Berlin, **1932**, 130.

[8] Staudinger, "Die Hochmolekularen, Organischen Verbindungen-Kautschuk und Cellulose," Berlin, **1932**, 134.

[9] Staudinger, *Kautschuk*, **6**, 153 (1930); Staudinger, "Die Hochmolekularen Organischen Verbindungen-Kautschuk und Cellulose," Berlin, **1932**, 404.

[10] Concerning the complex state of solution of heteropolar solvents, see Staudinger, "Die Hochmolekularen Organischen Verbindungen-Kautschuk und Cellulose," Berlin, **1932**, 333.

[11] McBain, *Nature*, **1935**, 1033; *Ind. Eng. Chem.*, **28**, 472 (1936).

[12] Staudinger, "Die Hochmolekularen Organischen Verbindungen-Kautschuk und Cellulose," Berlin, **1932**, 59.

[13] Staudinger and Heuer, *Z. physik. Chem.*, **171A**, 129 (1934); de Jong, Kruyt, and Lens, *Kolloidchem. Beih.*, **36**, 429 (1932).

[14] Here only solutions of homopolar substances in homopolar solvents are concerned, and therefore those cases where coördinated molecules are formed in solution, as with acids, alcohols, and similar compounds with secondary valences, are disregarded.

[15] Staudinger, *Naturwissenschaften*, **1934**, 65; Staudinger and Heuer, *Z. phys. Chem.*, **171A**, 129 (1934).

[15a] Staudinger and Heuer, *Ber.*, **62**, 2933 (1929).

[16] These hydrorubbers were obtained through the kindly aid of the management of the I. G. Farbenindustrie, Ludwigshafen.

[17] The molecular weight determinations of these hydrorubbers are described in the 45th Communication, *Kautschuk*, **12**, 159 (1936).

[18] Staudinger, "Die Hochmolekularen Organischen Verbindungen-Kautschuk und Cellulose," Berlin, **1932**, 135.

[18a] The values of K_m are taken from Table III of the 44th Communication of this Series, *Kautschuk*, **12**, 123 (1936); those of y from Table II of the 45th Communication, *Ibid.*, **12**, 160 (1936).

[19] Staudinger and Heuer, *Z. phys. Chem.*, **171A**, 129 (1934).

[19a] The K_m constant is higher in solvents in which the molecules are especially highly solvated.

[20] Staudinger and Leupold, *Ber.*, **67**, 304 (1934).

[21] The crepe rubber used in this investigation was furnished by the I. G. Farbenindustrie, Leverkusen.

[22] Staudinger and Mojen, *Kautschuk*, **12**, 159 (1936); Kirchhof, *Kolloid-Z.*, **15**, 30 (1914).

[23] *Kolloid-Z.*, **49**, 140 (1929).

[24] *Ber.*, **63**, 734 (1930).

[25] *Kolloid-Z.*, **12**, 143 (1913).

[26] *Kolloidchem. Beih.*, **10**, 85 (1919).

[27] *Ber.*, **63**, 921 (1930).

[28] The K_m values are taken from the 44th Communication of this series, *Kautschuk*, **12**, 123 (1936); the constant was not determined for C_6H_5Cl, but was assumed to be 3.7×10^{-4}, as for C_6H_6 and tetralin.

[Translated for Rubber Chemistry and Technology from Kautschuk, Vol. 13, No. 3, pages 39–41, March, 1937.]

Isoprene and Rubber

Part 47.[1] The Decomposition of Rubber by Acids

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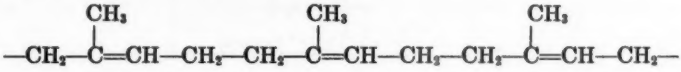
Introduction

In attempts to prepare rubber hydrochloride, C. O. Weber[2] observed that the viscosity of chloroform solutions of rubber which were employed in his work diminished considerably. Later this phenomenon was confirmed by Kirchhof,[3] who called particular attention to the fact that very small proportions of acids are sufficient to lower considerably the viscosity of rubber solutions. Extensive experiments on this subject have been carried out by Eggink and de Vries[4] and at about the same time by Whitby,[5] who studied the effect of adding inorganic and organic acids to benzene solutions of rubber. Likewise these investigators confirmed the observations of Weber mentioned above. Of interest also are experiments by Spence and Kratz,[6] who added 0.5 per cent of trichloroacetic acid to a benzene solution of rubber, in an attempt to obtain a rubber solution which would have the lowest possible viscosity at high concentrations of rubber; at the same time they attempted to separate the soluble components from the insoluble components of the rubber.

All these experiments are based on the idea, prevalent at the time, that rubber has a micellar structure; and the phenomena observed were attributed to changes in this micellar structure. Thus, Spence and Kratz wrote that "Viscosity is not a definite value, as is so frequently assumed by so-called rubber experts, but varies within very wide limits as a result of frequently uncontrollable causes. For instance, we have found first of all that the presence of a mere trace of acid reduces enormously the viscosity of a rubber solution."

The researches of Staudinger[7] and his collaborators over a period of years showed that the high viscosities of rubber solutions are attributable, not to the presence of micelles, but to the shape of the molecules of rubber, which may be represented as long rods of the following structure:



Isoprene molecules are the building stones of these little rods, the linking of about 2000 of these stones into a chain giving rise to macromolecules of rubber. On this basis a single particle has a molecular weight of approximately 140,000, and a length of approximately 16,000 A. U. It should however be pointed out that these chains are not all of the same length, and natural rubber is composed of a mixture of homologous polymers of differing chain lengths.[8]

Decomposition of Dissolved Rubber

Rubber molecules are extraordinarily sensitive to oxidizing agents, and because of the widespread destruction of the fiber molecules brought about by atmospheric oxygen,[9] experiments on rubber solutions are rendered very difficult. It has been

shown by Leupold[10] that even traces of oxygen in the solvents used in such experiments destroy the fiber molecules. Many years ago van Rossem and Fol observed that this demolition is catalyzed by light, for in darkness the viscosities of rubber solutions do not diminish.

The following graphical representation, which is taken from work by Leopold,

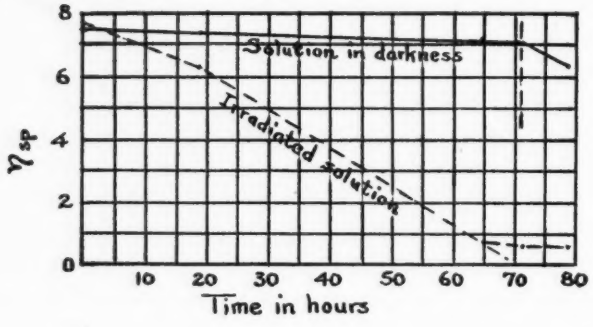


Figure 1—Changes in the Viscosity of a Rubber Solution in Light and in Darkness

shows the behavior of a rubber solution in air, both in light and in darkness. It is obvious that the rod-like molecules are not destroyed as long as the solution is protected from light. On exposure to light, however, the viscosity begins to diminish immediately.

In view of these facts, it seemed of particular interest to study the influence of

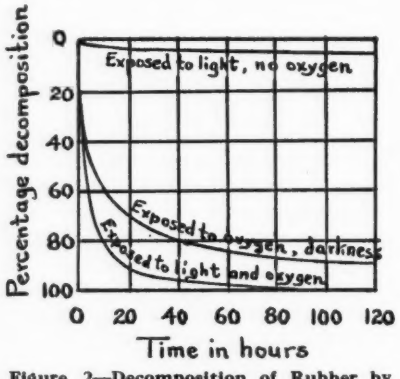


Figure 2—Decomposition of Rubber by Acids

very small proportions of acids on the decomposition of rubber. Because of the high molecular hydrocarbon structure of rubber molecules, it was not quite conceivable that acids can decompose these molecules, since they combine only at the double bonds of the hydrocarbon, and do not bring about a cleavage of the hydrocarbon molecule itself. Accordingly the changes in the viscosity of a rubber solution, to which 5 per cent of chloroacetic acid was added, were followed. The observation of Spence and Kratz was confirmed in this experiment, as may be seen

from Fig. 2, *viz.*, that the viscosity diminished greatly, so that extensive destruction actually takes place. This also happens in darkness, so that autoöxidative decomposition rather than cleavage of the rubber molecules by acids is involved, as is shown by the experiments described below. When oxygen is completely excluded, there is no change in viscosity, in spite of the presence of an acid. No decomposition therefore occurs, even when the solution is exposed to light throughout the experiment. The experimental results first described are to be attributed to the fact that the breaking up of the rubber molecules is catalyzed by acids and under these conditions it proceeds even in the absence of light. In the presence of acids, autoöxidation is not a photochemical process.

Similarly there was no decomposition when a 1.36 per cent balata solution (0.2 g. of balata)[13] was treated with four different acids at various concentrations, in the presence of light, with rigorous exclusion of oxygen. Here too, as in all experiments with rubber solutions, it is well to point out in passing that the solvent must be free of air.[14]

TABLE I

BEHAVIOR OF A 1.36 PER CENT SOLUTION OF BALATA WHEN VARIOUS ACIDS ARE ADDED, WITH EXCLUSION OF OXYGEN, BUT WITH EXPOSURE TO LIGHT

(Time of Reaction 24 Hours)

Series	Acid	Percentage	η_{sp}
I	Acetic acid	0	5.50
		1.2	5.18
		2.4	5.01
		4.8	4.84
II	Chloroacetic acid	0	5.50
		1.9	4.91
		3.8	4.59
		7.6	4.09
III	Dichloroacetic acid	0	5.44
		0.65	5.07
		1.29	5.13
		2.58	4.50
IV	Trichloroacetic acid	0	5.40
		0.82	4.61
		1.65	5.38
		3.30	5.44

Decomposition of Rubber in the Solid State

The natural antioxygens present in raw rubber in the solid state protect it to a certain extent against attack by oxygen,[15] on the other hand these antioxygens are decidedly inactive when the rubber is in solution. In view of this fact, the effect of acids in solid rubber was next studied. In these experiments, raw rubber was

TABLE II

ACTION OF CHLOROACETIC ACID AND TRICHLOROACETIC ACID ON SOLID RUBBER WITH EXCLUSION OF AIR AND LIGHT

(Time of Treatment 24 Hours)

Acid	Percentage Concentration	η_r	η_{sp} (1.4%)
None	0.0296	1.19	9.0
2% Chloroacetic acid	0.0272	1.17	8.8
	0.0364	1.20	7.7
2% Trichloroacetic acid	0.0144	1.08	7.9
	0.0256	1.15	8.2

swollen in ether, and small proportions of acids were added in such a way that the acids could diffuse into the rubber. The ether was then distilled away, and after these acidified samples had been allowed to stand 24 hours, their viscosities were measured with a view to determining the extent of decomposition. These viscosity measurements were carried out in the sol solution range, so that they could be utilized for calculating molecular weights. When light and air were excluded, there was no cleavage of the macromolecules, as was to be expected. The results of the experiments are shown in Table II.

A few samples which were exposed to light, but were protected from oxygen, behaved in a similar way when treated with acids. Table III shows that here too there was no decomposition.

TABLE III

ACTION OF CHLOROACETIC ACID AND TRICHLOROACETIC ACID ON SOLID RUBBER IN LIGHT BUT IN THE ABSENCE OF OXYGEN

(Time of Reaction 24 Hours)

Addition	Percentage Concentration	η_r	η_{sp} (1.4%)
None	0.0392	1.25	8.9
2% Chloroacetic acid	0.0296	1.16	7.6
2% Trichloroacetic acid	0.0388	1.16	7.8
2% Trichloroacetic acid	0.0412	1.27	9.2

In the other experiments, samples of rubber were protected from light but not from oxygen. In this series it was observed that the rubber was transformed into an insoluble, greatly swollen product. This sort of change is known also to take place when rubber is kept in light, and it has been studied at various times. Formerly it was ascribed to changes in the micellar structure of rubber,[17] but actually it depends on the effect of atmospheric oxygen, for when the latter is absent, no such changes occur. Consequently in this case too, autoöxidation must take place[18] in spite of the absence of light, with union of the fiber molecules by oxygen bridges.[19]

The results of this series of experiments are summarized in the Table IV.

TABLE IV

ACTION OF CHLOROACETIC ACID AND TRICHLOROACETIC ACID ON SOLID RUBBER IN THE PRESENCE OF AIR BUT IN THE ABSENCE OF LIGHT

(Time of Reaction 24 Hours)

Addition	Percentage Concentration	η_r	η_{sp}(1.4%)
None	0.0416	1.26	8.7
2% Chloroacetic acid	0.0428	1.26	8.7
	0.0416	1.26	8.7
2% Trichloroacetic acid	0.0436	Partially insoluble	
	0.0512	Partially insoluble	

TABLE V

ACTION OF CHLOROACETIC ACID AND TRICHLOROACETIC ACID ON SOLID RUBBER EXPOSED TO LIGHT AND IN THE PRESENCE OF AIR

(Time of Reaction 24 Hours)

Addition	Percentage Concentration	η_r	η_{sp}(1.4%)
None (without air and light)	0.0512	1.40	10.8
None	0.0400	1.16	5.4
2% Chloroacetic acid	0.0400	1.04	1.4
5% Chloroacetic acid	0.0400	1.01	0.5
2% Trichloroacetic acid	0.0400	1.05	1.7
5% Trichloroacetic acid	0.0400	1.01	0.4

In a final series of experiments, a study was made to ascertain the changes brought about in solid raw rubber by chloroacetic acid and by trichloroacetic acid when the acidified samples were exposed both to light and to air. Table V shows the expected results, *viz.*, that both acids bring about decomposition of the rubber to a considerable extent.

Summary

The phenomena observed in the experiments which have been described can be explained in the following way. As already mentioned, raw rubber contains certain antioxygens which protect the rubber molecules from attack by oxygen. Very little is known about the nature of these antioxygens, but it is probably correct to assume that these substances are of a basic nature, like commercial antioxygens, which for the most part are complex organic bases. The activity of these anticatalysts is stopped by the addition of organic or inorganic acids. As a result there is no longer any obstacle to an attack by oxygen, and decomposition can proceed under these conditions much more rapidly and much more extensively. The antioxygens are destroyed by the acids, even when oxygen is excluded during the experiments, but demolition of the fiber molecules does not then take place. The intense destructive effect of oxygen on rubber does not therefore depend on the action of acids on the fiber molecules of rubber, but is to be attributed solely to the fact that antioxygens which inhibit decomposition by oxygen are destroyed; destruction of the rubber itself is caused only by oxygen.

It is not impossible that these phenomena bear a close relationship to the stickiness acquired by rubber. Rubber which has become sticky is composed of extensively decomposed rubber molecules. This phenomenon is noticeable at times in rubber goods which have been stored for a long time, and may be explained by the fact that atmospheric carbon dioxide destroys the natural antioxygens in the rubber. With their destruction, atmospheric oxygen then has free play to attack the rubber molecules. The acidic substances which are formed in this oxidation then destroy any remaining antioxygens, so that oxygen can destroy all of the rubber.

Grateful acknowledgment is due Professor Staudinger, at whose instigation this work was carried out, who offered advice in various ways, and who took an active part in the investigation.

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[8] Staudinger, *Ibid.*, Aug., 1925, 5; Sept., 1925, 8; *Ber.*, **59**, 2019 (1926).

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[12] Fol, *Kolloid-Z.*, **12**, 144 (1913).

[13] In these experiments balata was employed because it is far more easily purified than is rubber and furthermore its behavior is quite analogous to that of rubber.

[14] Staudinger and Leopold, *Ber.*, **63**, 730 (1930).

[15] Dufraisse and Drisch, *Rev. gén. caoutchouc*, **8**, No. 71, 9 (1931); Bruson, *Ind. Eng. Chem.*, **19**, 1187 (1927); Bondy, *Ber.*, **66**, 1611 (1933).

[16] Staudinger, *Kautschuk*, **6**, 153 (1930).

[17] Bary and Hauser, *Ibid.*, **4**, 96 (1928).

[18] It must however be pointed out that this phenomenon differs somewhat from cyclization (cf. Staudinger and Widmer, *Helv. chim. acta*, **9**, 529 (1926)), which Kirchhof (*Kolloid-Z.*, **30**, 183 (1922)) observed in the action of concentrated sulfuric acid on rubber.

[19] Staudinger and Bondy, *Ann.*, **488**, 153 (1931); Staudinger "Die Hochmolekularen Organischen Verbindungen-Kautschuk und Cellulose," Berlin, **1932**, 442.

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Some Physical Properties of Isoprene

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INTRODUCTION

Isoprene (2-methyl-1,3-butadiene) has been for many years a substance of very considerable interest in the study of rubber, since it has been shown to be the fundamental unit in the constitution of the rubber hydrocarbon. Isoprene polymerizes to form a product which is chemically more closely related to natural rubber than any other synthetic product.[9, 20, 33, 35, 48, 53, 56] Furthermore, the destructive distillation of natural rubber yields as its two major products isoprene and dipentene (*dl*-1-methyl-4-isopropenyl-1-cyclohexene) in amounts far exceeding those of any other constituents.[4, 30, 56] Aside from its relation to rubber, isoprene is of interest, because it is thought to be the basic substance in the natural synthesis of terpenes and to play an important role in the formation of plant cells.[3, 8, 13, 49, 50, 54]

An investigation of the chemical thermodynamics of rubber now in progress at the Cryogenic Laboratory of this Bureau includes a study of isoprene and its relationship to rubber. Measurements of heat capacity and heat of combustion are at present being made on isoprene for the purpose of calculating its entropy. A report covering these results is now being prepared. Similar measurements for rubber have already been reported.[5]

Since samples of high purity were desired for this work, care was taken in the preparation and purification of the isoprene, and the resulting product is thought to represent an improvement in purity compared with isoprene prepared by previous investigators. Furthermore, not all workers realized the importance of working with freshly purified samples. Also it is now possible to take advantage of recent important improvements in the technic of measuring physical properties, especially boiling point and related properties. In view of the wide divergence of values for many of the commonly measured physical properties, as reported in the literature, it seems worth while to report the values here obtained with samples of high purity.

PREPARATION AND PURIFICATION OF SAMPLE

The isoprene was made by the cracking of dipentene vapor by means of the "isoprene lamp" method of Harries and Gottlob[22] as modified by Whitby and Crozier.[55] About 5.5 liters of crude isoprene was prepared, which had a yellow color and possessed a sharp odor. It was then subjected to successive distillations. The vacuum-jacketed column used was about 140 cm. in height, and included 40 bulbs with ball valves and side tubes, according to the design of Swietoslawski.[39,40] The column head included a dephlegmator and condenser, with take-off so arranged that the reflux ratio could be adjusted by means of drop-counters. For the isoprene distillation, a 15 to 1 ratio was generally maintained. Temperature changes were read to the nearest 0.001° C. by means of a Beckmann-Swietoslawski mercury thermometer[41] immersed in a mercury well surrounded by vapor rising from the dephlegmator. Corrections in the distilling temperature of the isoprene were made

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for changes in barometric pressure by simultaneous observations of the boiling point of pure water in a barometric ebulliometer.

Three successive distillations were made, with a reduction of charge in each case to include only the most nearly constant-boiling part of the previous distillation. Isoprene was evidently present in far greater amounts than any other substance. The impurities were very largely materials of boiling points lower than that of isoprene, some of them condensing only at the temperature of solid carbon dioxide. In the early fractions of the first distillation, water was distilled over in small amounts as a separate phase. When the first distillation was continued above the boiling point of isoprene, no significant approach to constancy of boiling point was obtained below 176° C., the approximate boiling point of dipentene. It was therefore concluded that the cracking process had yielded practically no substances with boiling points between those of isoprene and dipentene, and that the crude isoprene had contained some unchanged dipentene.

The third and final distillation yielded 200 cc. of a product distilling within a range of 0.01° C. The sample was colorless and possessed only a slight odor. This fraction was thoroughly mixed, and different portions were used immediately in the determination of physical properties, several measurements being performed simultaneously.

PHYSICAL PROPERTIES

A number of previous observers have noted that isoprene on standing for months or years at room temperature under atmospheric conditions will oxidize and polymerize.[1, 11, 12, 26, 44, 55] For this reason the physical properties here reported were determined as soon as possible after the final distillation. With the exception of the freezing point and expansivity, all measurements were made within 5 hours after the end of the final distillation. The sample used in the freezing-point determination had been kept in a refrigerator at about 8° C. for 2 days, while that used in determining the expansion was several weeks old.

The expansivity, however, is thought to change only slightly with change in purity. In order to obtain some idea of the rate of polymerization, a sample which had been kept at 8° C. for 2 months was distilled, and a solid residue amounting to less than 0.5 per cent of the weight of the sample was obtained.

Degree of Purity

Swietoslawski[42] has set up for comparative purposes an arbitrary scale for the degree of purity of liquids. This scale is based on the measurement of Δt, the difference between the temperature of the boiling liquid and the temperature of the condensing vapor, determined in a differential ebulliometer of standard dimensions. For a pure substance Δt is zero, and increases with increased concentration of impurities.

The freshly prepared sample of isoprene from the third distillation was found to have a Δt of 0.002° C. This value falls within the limits of the fifth or highest degree on the purity scale (range from 0.000° to 0.005° C.). A sample of isoprene from the previous distillation was found to have a Δt of 0.006° C. Its purity then was of the fourth degree (range from 0.005° to 0.020° C.). This sample was left in the ebulliometer at room temperature for 2 weeks. At the end of this time its Δt value had increased to 0.028° C., and its purity had decreased to the third degree (range from 0.020° to 0.050° C.). This increase in Δt is direct confirmation of the expected decrease in purity brought about by oxidation and polymerization of the isoprene.

Changes with time in other physical properties as mentioned below are other evidences of change in the material.

Boiling Point and Its Relation to Pressure

The normal boiling point of isoprene was determined in the ebulliometer used for the purity determination, following the comparative method of Swietoslawski.[43] According to this procedure a second ebulliometer containing pure boiling water is connected, together with the first ebulliometer, to a closed system in which the pressure can be adjusted. Determinations of the boiling point, by observing the temperature of the boiling liquid in equilibrium with the vapor, were made for both liquids under at least three different pressures, including values both above and below 760 mm. of mercury. The temperatures were measured with a Mueller[31] type of Wheatstone bridge and a resistance thermometer designed for precise temperature measurements,[29] and calibrated in accordance with the procedure for the International Temperature Scale.[10]

In order to obtain the normal boiling point of isoprene from the observations, it was merely necessary to find the boiling point of isoprene under the pressure at which the boiling point of water would be exactly 100° C., since that pressure is exactly 760 mm. by definition of the temperature scale. This procedure avoids the loss of precision inherent in the corrections to be applied to the readings of a mercury barometer.

For a sufficiently small range of pressures near the normal boiling points, the relation between t_s, the boiling point of an organic substance, and t_w, the boiling point of water under the same pressure, can be represented by a function of the second degree; hence its derivative, $\frac{dt_s}{dt_w}$, changes linearly with change of pressure when this pressure is defined by the boiling point of water.[58] It was found that the quotient of finite increments, $\frac{\Delta t_s}{\Delta t_w}$, evaluated at the midpoints of several small intervals, changed only about 0.2 per cent for a 2° C. change of t_w. The ratios $\frac{\Delta t_s}{\Delta t_w}$ were

TABLE I

DEGREE OF PURITY, BOILING POINT, AND CHANGE OF BOILING POINT WITH CHANGE OF PRESSURE FOR SEVERAL SAMPLES OF ISOPRENE

Δt[a] °C.	Degree of Purity	$\frac{dt_s}{dt_w}$[b]	Boiling Point of Water °C.	$\left(\frac{dt}{dP}\right)_s$[c] °C./mm.	Normal Boiling Point of Isoprene Sample °C.
0.028	Third	....	.....	0.0383	34.124
0.006	Fourth	....	.....	....	34.102
0.002	Fifth	[d]1.0367 [f]1.0359 [h]1.0338	[e]100.720 [g]100.000 [i] 97.988	0.0382	34.076

[a] Difference between the boiling temperature of isoprene and its condensation temperature in a differential ebulliometer of standard dimensions.

[b] Ratio of the change in boiling point of isoprene to that of water for the same change in pressure.

[c] Change of boiling point of isoprene per millimeter change of pressure at 760 mm.

[d] At midpoint between t_s and t''_s.

[e] $\frac{t''_w + t_w}{2}$.

[f] Interpolated value.

[g] Defining 760 mm. pressure.

[h] At midpoint between t'_s and t_s.

[i] $\frac{t'_w + t_w}{2}$.

evaluated at the midpoints between t'_w and t_w, and t''_w and t_w, respectively; t_w being a measurement close to 760 mm. pressure, t'_w below, and t''_w above this pressure. The derivative $\frac{dt_s}{dt_w}$ at 100.000° C. was obtained by interpolation. These values are given in Table I. The normal boiling point, t_B, is then calculated[57] from the observed values of t_s and t_w by the equation

$$t_B = t_s + \frac{dt_s}{dt_w}(100.000 - t_w)$$

The estimated probable error in the normal boiling point, 34.076° C., based on three determinations of this kind, is ±0.003° C.

The value of $\frac{dt}{dP}$, the change of boiling point of isoprene with change of pressure at 760 mm. of mercury, was obtained by multiplying the value of the derivative

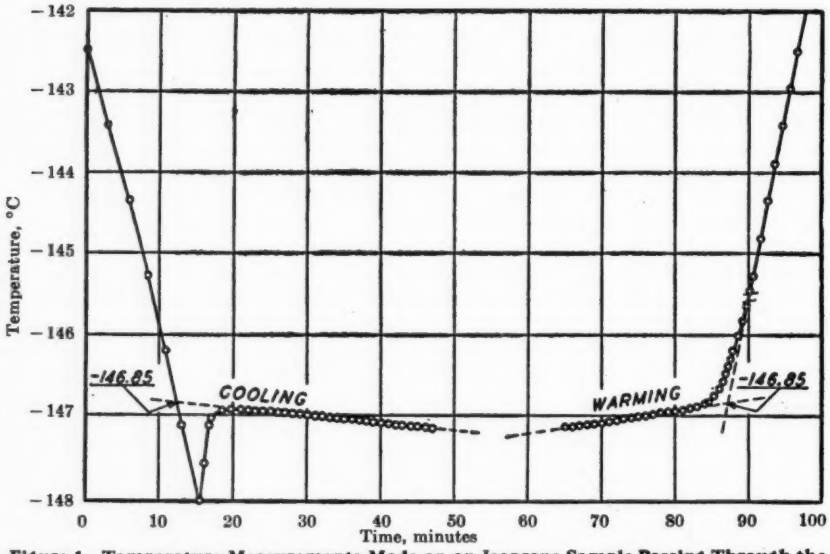

Figure 1—Temperature Measurements Made on an Isoprene Sample Passing Through the Liquid-Solid Transition, Both Cooling and Warming

$\frac{dt_s}{dt_w}$, at 760 mm. by 0.369, which is the value in degrees per millimeter for the change of boiling point of water at 760 mm.[32] The value for isoprene was thus found to be 0.0382° C. per millimeter of mercury. Table I also shows the data and results of these determinations. For the purpose of comparison some values are also given for samples of lower purity. Higher boiling points and larger values of $\frac{dt}{dP}$ are characteristic of less pure samples.

Freezing Point

The freezing point of isoprene was measured in accordance with the procedure of Mair,[28] using apparatus essentially similar to that described by him.

The isoprene was contained in a double-walled glass tube, the inner space between the walls being evacuated. Temperatures were measured with the same platinum resistance thermometer used for the boiling-point determination. Mechanical stirring with the spiral wire surrounding the thermometer and operated by an electric motor was continued throughout the determination.

The data for the freezing- and melting-point determinations are plotted in Fig. 1. The freezing point, determined as the temperature of the intersection of the freezing curve with the normal cooling curve, agrees with the melting point determined in a similar manner from the melting and the normal warming curves. The estimated error in the value −146.8° C. is thought not to exceed ±0.2° C. The variation obtained in repeated observations on a single sample was considerably less than 0.2° C. but was of this order between different samples. Preliminary results of somewhat less precise melting-point determinations made in the course of heat-capacity measurements on a different sample using quite different apparatus and technic gave a value of − 146.6° C.

Volume Expansivity

The volume expansivity, or temperature coefficient of volume expansion, $\frac{1}{V}\frac{dV}{dt}$, in which V is the volume at the centigrade temperature t, was determined by dilatome-

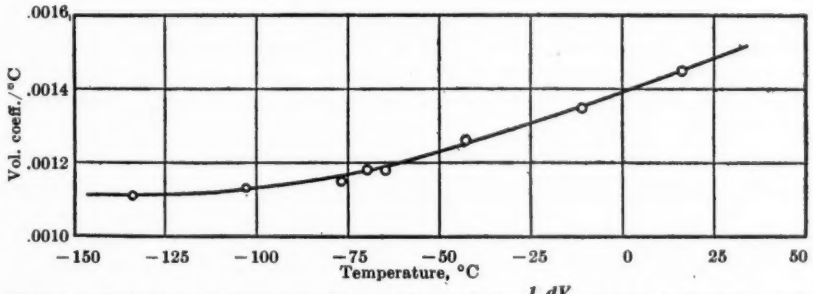

Figure 2—Relation Between the Volume Expansivity, $\frac{1}{V}\frac{dV}{dt}$, of Liquid Isoprene and Temperature

ter measurements extending from temperature near the freezing point almost to the boiling point. The dilatometer, made of low-expansivity glass, had a bulb with a volume of 22.31 cc. capacity, joined to a capillary about 40 cm. in length with an average volume of 0.02276 cc. per centimeter. A temperature range of about 20° C. was covered in each run. For each run there was plotted a graph of the height of the liquid in the capillary as a function of the temperature. The temperature range was so small that no significant deviations from linearity over a single run could be observed. From the slope of the graph and the dilatometer dimensions, the expansivity at the mean temperature of each run was calculated. These values have been plotted in Fig. 2, each point representing a separate run.

Four terms were necessary in a power series in order to express the expansivity to within 1 per cent over the whole range of temperature, as given in the following equation:

$$\frac{1}{V}\frac{dV}{dt} = -\frac{d\rho}{\rho dt} = 1.393 \times 10^{-3} + 3.63 \times 10^{-6}t + 5.35 \times 10^{-9}t^2 - 38.8 \times 10^{-12}t^3$$

For temperatures above −100° C. this equation yields values agreeing with the observed expansivity to better than 0.5 per cent. An integration of the preceding equation, together with the expansion of an exponential, leads to the following equation:

$$V = V_0(1 + 1.393 \times 10^{-3}t + 2.79 \times 10^{-6}t^2 + 4.31 \times 10^{-9}t^3 - 5.60 \times 10^{-12}t^4)$$

in which V_0 is the volume at 0° C.

Density

The density of a sample of the purest isoprene was determined by E. R. Smith of this Bureau, using a quartz picnometer of a type previously described.[36,51] The temperature was thermostatically controlled at 20.00 ± 0.02° C. Since the picnometer had a capillary of about 0.1 mm. diameter and was closed with a ground-glass joint, the evaporation correction, made by extrapolation of the observed change of weight with time, was very small. The value actually obtained for the density was 0.68053 g. per cc. In view of the uncertainties caused by the change of the material with time, as noted below, the value is rounded off and reported as 0.6805 ± 0.0001 g. per cc. From the density of the isoprene at 20° C. and the expansivity data, the following equation may be derived for the density, ρ, of liquid isoprene at any temperature, t:

$$\rho = 0.7002 - 0.9754 \times 10^{-3}t - 0.592 \times 10^{-6}t^2 + 0.525 \times 10^{-9}t^3 + 9.66 \times 10^{-12}t^4$$

After storage for 24 hours at 8° C. the value obtained for the same sample at the same temperature had risen from 0.6805 to 0.6808 g. per cc. Values on the two succeeding days were 0.6814 and 0.6819 g. per cc., respectively. This continuous rise in density is further evidence of the change brought about by oxidation and polymerization.

Calculation of Heat of Vaporization

The Clausius-Clapeyron equation can be used for the calculation of the latent heat of vaporization of isoprene when the previously determined constants are used together with the specific volume of the vapor at the boiling point. Measurements of the specific volume have not been made, but an approximate value can be calculated. Normal pentane and isopentane are the liquids most similar to isoprene for which data on critical temperatures and pressures are available. For each of these at the boiling point the "reduced temperature,"[27] or ratio of temperature to critical temperature, is about 0.65. Also for each of these at the normal boiling point the "reduced pressure," or ratio of pressure to critical pressure, is about 0.030. Since there is very little difference in the "reduced" states at the boiling point for similar organic compounds, these may be presumed to be the approximate values for isoprene at its boiling point.

Lewis[27] has recently published graphs, applicable to any hydrocarbon with more than three carbon atoms per molecule, which yield as a function of the "reduced" states the value of μ, defined as PV/RT, in which P and V are, respectively, the pressure and volume of 1 mole of vapor, R is the universal gas constant, and T the absolute temperature. For the above values of the "reduced" temperature and pressure, Lewis' graph indicates a value of 0.96 for μ. In other words, at the boiling point the specific volume of isoprene vapor is 96 per cent of the specific volume of an ideal gas of the same molecular weight and at the same temperature and pressure. (Direct observations on n-pentane and isopentane at their boiling points, yield values of μ within 1 per cent of 0.96.) The specific volume of an ideal gas of the same molecular weight as isoprene at 34.076° C. and under a pressure of 760 mm.

is 371 cc. per g. The specific volume of isoprene vapor under the same conditions is therefore 356 cc. per g.

In the Clausius-Clapeyron equation

$$L = \frac{T(V_v - V_l)}{\frac{dt}{dP}}$$

L is the latent heat of vaporization of 1 g. of liquid; T, the boiling point, 307.2° K.; V_v, the specific volume of the vapor, 356 cc. per g.; V_l, the specific volume of the liquid calculated from the previous values for density and expansivity. 1.5 cc. per g.; and $\frac{dt}{dP}$, the rate of change of boiling point with change of pressure as previously measured, 0.0382° C. per millimeter (or 28.7×10^{-6}° C. per dyne per cc.). The latent heat of vaporization of isoprene at the normal boiling point is thus calculated to be 380 j. per g. (90.8 cal. per g.) or 25.9 kj. per mole (6.17 kcal. per mole). Because of the uncertainity in the value of the specific volume of the vapor the estimated probable error in the calcuation is ± 1 per cent.

The Bingham-Nernst modification[6] of Trouton's rule is

$$\frac{L_m}{T_B} = 17 + 0.011T_B$$

in which L_m is the molal latent heat of vaporization in calories, and T_B the absolute temperature of the boiling point. The right-hand member of the equation has the value 20.4, and the left-hand member 20.1. The rule in this form appears to be valid for isoprene within the limits of precision of determination of the heat of vaporization. This is taken as evidence that isoprene in the liquid form is not associated.

Refractive Index and Molecular Refraction

Measurements of refractive index at temperatures from 9° to 30° C. were made with a water-jacketed Abbé refractometer (Valentine model) calibrated with distilled water. The values obtained are plotted in Fig. 3, from which the refractive index at 20° C. is found to be 1.42160 ± 0.00005, and the change with change in temperature -0.656×10^{-3} per degree centigrade. Therefore, the index of refraction, n_D, at temperature, t, is

$$n_D = 1.43472 - 0.656 \times 10^{-3}t$$

This equation is applicable for liquid isoprene at least over the range from 9° to 30° C., and probably over a wider range. The refractive indices of fractions boiling both below and immediately above the purest isoprene were lower than that of the isoprene. The property is, however, not sensitive to very small amounts of impurities having boiling points near that of isoprene, since the third distillation, which lowered Δt from 0.0060 to 0.002° C., raised the refractive index only by about 0.00001.

Oxidation and polymerization of the isoprene on standing, however, brought about progressive increases in refractive index. For the first few days the daily changes were of the order of 0.0002. Later the rate of increase became considerably less, and rather variable. At the end of 2 months the total increase was about 0.00450, and the material had become so lacking in homogeneity that further measurements were impossible.

The molecular refraction is often calculated by summing up the refractions of the individual atoms and adding a certain quantity for the "exaltation" due to double bonds or other special features of the structure. In the present case, however, no precise calculation is possible because the exaltation due to the conjugated double bond varies considerably from one compound to another. From the Lorenz-Lorentz formula, using the refractive index and density values as determined in this investigation, the molecular refraction is computed to be 25.39. By taking this value for the molecular refraction, and 2.490 and 1.066 for the atomic refractions of carbon and hydrogen, respectively, as reported by Swietoslawski,[38] the exaltation due to the conjugated system in isoprene is 4.41. This is not greatly different from 4.32 for the conjugated system in 2,3-dimethyl-1,3-butadiene and 3.98 for chloroprene (2-chloro-1,3-butadiene).

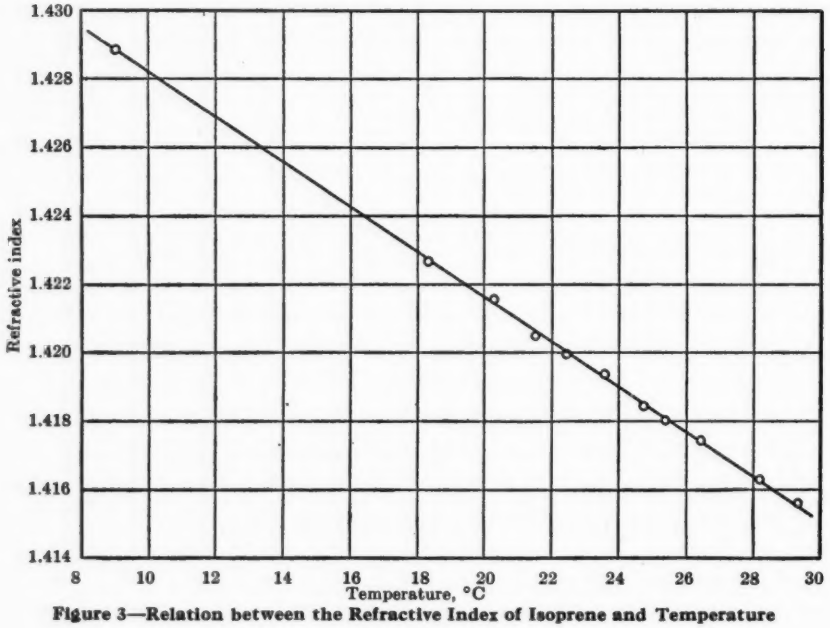

Figure 3—Relation between the Refractive Index of Isoprene and Temperature

The molecular refraction is commonly thought to be practically independent of temperature over moderate ranges. If this is true, differentiating the Lorenz-Lorentz equation gives in the resulting equation a relation between the change of refractive index with change of temperature and the expansivity

$$\frac{dn}{dt} = -\frac{(n^2+2)(n^2-1)}{6n}\left(\frac{dV}{V dt}\right)$$

At 20° C. the observed expansivity is 1.467×10^{-3} per degree centigrade and the observed refractive index is 1.42160. These quantities yield a numerical value of 0.705×10^{-3} for the right-hand member of the above equation. This is to be compared with 0.656×10^{-3}, the directly observed value of the left-hand member. This agreement is only fair, but it is of interest to note that both values are considerably

higher than those given for most organic liquids, for which the average is about 0.45 $\times 10^{-3}$.

COMPARISON WITH PREVIOUS INVESTIGATIONS

The boiling point, density, and refractive index of isoprene have been determined by many investigators, and the more significant results are given in Table II. For the purpose of comparison, the boiling points have been converted, wherever possible, to those at 760 mm. pressure. Also the original values of density and refractive index have been converted to those at 20° C.

TABLE II

COMPARISON OF THE DATA OF VARIOUS INVESTIGATORS ON SOME PHYSICAL PROPERTIES OF ISOPRENE

Observers	Year	Reference Number	Boiling Point at 760 Mm. ° C.	Density at 20° C. g/ml.	Refractive Index at 20° C.	Freezing Point ° C.
Williams	1860	[56]	37 to 38[a]	0.6811	.....	...
Tilden	1882	[47]	34 to 35[a]	....	.....	...
Gladstone[c]	1886	[18]	.....	0.6681	1.4028	...
Thorpe and Jones	1893	[45]	35.5 to 36.1[a]	0.6714	.....	...
Thorpe and Rodger	1894	[46]	35.5 to 37.0[a]	....	.....	...
Perkin	1895	[34]	36	0.6717	.....	...
			36 to 37	0.6696	.....	...
Ipatiew[c]	1897	[24]	32 to 33[a]	0.6722	1.40646	...
Euler	1897	[16]	33 to 39[a]	....	.....	...
Blaise and Courtot	1906	[7]	36[a]	....	.....	...
Harries and Gottlob	1911	[22]	35 to 37[a]	....	.....	...
Harries	1911	[21]	30 to 37[a]	0.676	1.41205	...
			36 to 37[a]	0.6800	1.42333	...
			35.5 to 36.0[a]	0.6803	1.42019	...
Lebedew and Skawronski	1913	[26]	34.5 to 35.0	0.6803	1.42207	...
Kucherov	1913	[25]	.....	0.6803	.....	...
Harries	1914	[19]	33.7 to 33.9	0.6832	1.42387	...
Steimmig	1914	[37]	33.5 to 34.0[a]	0.6760	.....	...
Aschan	1915	[2]	34.1 to 34.6	0.6811	1.41540	...
Enklaar	1916	[15]	.....	....	.....	About −120
Enklaar	1916	[14]	33.9 to 34.4	0.6809	1.41786	...
Waterman and van Westen	1929	[52]	34.4 to 34.9	0.6806	1.4194	...
Conant and Tongberg	1930	[11]	36 to 38[a]	0.68	.....	...
Heisig	1931	[23]	33.7 to 34.1	....	.....	...
Farmer and Warren	1931	[17]	34.4 to 35.8	0.6828	1.42093	...
Whitby and Crozier	1932	[55]	34.0 to 34.5	....	.....	...
Bekkedahl, Wood, and Wojciechowski	1936	..	34.076	0.6805	1.42160	−146.8

[a] Atmospheric pressure not recorded.
[b] Measurements made by Harries. See reference [21].
[c] Sample of isoprene obtained from Tilden.

Because of inadequate knowledge of the purity of the samples of previous workers, it is difficult to make a critical evaluation of the importance of their measurements. Incomplete removal of low-boiling impurities would be likely to lead to low values of the boiling point, density, and refractive index; oxidation and polymerization, on the other hand, to lead to high values. Almost all previous determinations of the boiling point have been observations of the range of temperature during distillation, and the values obtained depend greatly on the rate of distillation as well as the purity of the substance distilled, and give in most cases the condensation tem-

perature. With such a low-boiling liquid superheating of the vapor is very probable except in apparatus especially designed to avoid it.

The only freezing point determination recorded in the literature appears to be that of Enklaar,[15] who made visual observations of a small sample attached to a pentane thermometer. The resulting value, given as "about −120° C.," is considerably higher than that here obtained. Enklaar was unable to observe any distinct melting point.

The thermal expansion of isoprene was measured by Thorpe and Jones[45] in 1893 over a range of temperature from 0° to 32.6° C. The volume relation is given as $V = V_0(1+1.4603\times10^{-3}t+0.99793\times10^{-6}t^2+56.0149\times10^{-9}t^3)$. The coefficient of t is about 4 per cent higher than the value here reported. The other coefficients show little correlation, probably because of the difference in the ranges of temperature involved.

Perkin[34] determined densities of his isoprene samples at various temperatures from 4° to 25° C. From these values an expansivity of 1.43×10^{-3} is obtained for a temperature 12° C. This is in very good agreement with the value 1.437 for the same temperature, calculated from the equation determined in this investigation.

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Note on the Diffraction of X-Rays by Old Specimens of "Frozen" Rubber[1]

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Introduction

The object of the present note is to make available in the literature a detailed comparison of the x-ray diffraction effects from old specimens of "frozen" rubber with available data for stretched fresh rubber. Several x-ray diagrams of "frozen" rubber have been published,[2,3] and Ott[6] has recorded measurements made on a photograph of apparently "frozen" crepe. Although Ott's values have been confirmed in Clark's laboratory,[1] they appear to be the only values readily available in the literature, and are rather meagre.

Discussion

The two specimens that form the subject of the present note were examined for G. S. Whitby, and were supplied by him. They will be designated *A* and *B*. *A* was a pale thin unsmoked sheet made in the Malay States in 1905 and kept in the Imperial Institute, London, until it was turned over to Dr. Whitby in 1925. It was then in the "frozen" condition, and has therefore been in this condition for at least 11 years and probably for 30 years. *B* was a piece of smoked sheet made by G. S. Whitby in 1913, and has certainly been in the "frozen" condition for 22 years. The "thawing point" of both samples was approximately 41° C. This is the temperature at which, after heating for two hours, the samples lose their stiffness and become clear. The densities (15°/15°) of these "frozen" specimens were: *A*, 0.9436; *B*, 0.9347. After "thawing," by heating at 50° C. for two and one-half hours, the densities (15°/15°) dropped to—*A*, 0.9233; *B*, 0.9184. The writer is indebted to G. S. Whitby for the density determinations. As a test of this "thawing" procedure, a sample of *A*, after being photographed in the "frozen" condition, was suspended in water at 50° C. for two and one-half hours and then rephotographed. The well defined powder-pattern characteristic of diffraction diagrams obtained from "frozen" rubber was found to have been replaced by the strong single halo characteristic of unstretched fresh rubber. The spacing corresponding to this halo was about 4.7 A. U., compared with 4.5 A. U. reported by Katz[3] for "thawed" rubber, and 4.6 ± 0.1 A. U. reported by Mark and von Susich[5] for fresh unstretched rubber. The weak halo at 8.0 A. U., also observed by Mark and von Susich, does not appear in the present photograph.

Identical diagrams consisting of 13 sharply defined haloes were obtained from the two "frozen" specimens *A* and *B*. In general characteristics the photographs are typical of those usually obtained from finely powdered organic crystals.

Results

The x-ray data are summarized in the Table below, first column, present note (specimens *A* and *B*); second column, Ott's values[6] for "frozen" rubber; third

column, corresponding figures of Mark and von Susich[5] for stretched fresh rubber; fourth column, more recent data of Lotmar and Meyer[4] for stretched fresh

SUMMARY OF RESULTS

A and *B*	Ott [6]	Mark and von Susich[5]	Lotmar and Meyer[4]
0.123 *s.*	0.121 *w.*	0.1251 *v.s.*	0.1225 *s.*
...	...	...	0.140 *v.w.*
0.155 *v.s.*	0.153 *s.*	0.156 *s.*	0.154 *s.*
0.183 *v.s.*	0.182 *s.*	0.1851 *v.s.*	0.182 *v.s.*
		0.189 *m.*	0.188 *m.*
		0.194 *v.s.*	...
0.206 *s.*	0.192 *w.*	0.208 *m.*	0.205 *m.s.*
		0.212 *w.*	0.208 *w.*
0.226 *m.*	0.224 *w.*	0.227 *m.*	0.223 *w.*
		0.228 *m.*	0.223 *m.*
0.255 *w.m.*	0.240 *v.w.*	0.248 *m.*	0.245 *w.*
		0.262 *w.*	0.256 *w.*
0.277 *w.*	0.265 *v.w.*	...	0.270 *v.w.*
		0.279 *w.*	0.277 *w.*
		...	0.299 *v.w.*
0.298 *m.*	0.289 *v.w.*	0.293 *v.w.*	0.300 *v.w.*
		0.300 *w.*	0.299 *w.*
		0.308 *w.*	...
0.319 *v.w.*	...	0.323 *v.w.*	0.322 *v.w.*
...	...	...	0.336 *v.w.*
0.345 *w.m.*	...	0.350 *w.*	0.345 *v.w.*
		...	0.350 *v.w.*
		...	0.370 *w.*
0.372 *w.m.*	...	0.375 *m.*	...
		...	0.374 *v.w.*
0.398 *w.*	...	0.388 *w.*	0.400 *v.w*
0.418 *v.w.*	...	...	...

Debye-Scherrer Rings from an Old Sample of "Frozen" Raw Rubber

rubber. Data are recorded in terms of sin θ values for $Cu_{K\alpha}$ ($\lambda = 1.54$ A. U.) radiation; the figures of Ott (iron target, $\lambda = 1.93$ A. U.) were recalculated for copper, and those of Lotmar and Meyer (sin θ/λ) were multiplied by $\lambda(1.54)$. Visually

estimated intensities are indicated (m = medium, s = strong, v = very, w = weak). The brackets in Columns 3 and 4 serve to group fiber spots, which would lead to powder haloes unresolvable at the crystal-to-plate distances employed for the data of the first two columns. It will be seen that the agreement among the four columns is very good, and that the present more definite powder photographs of "frozen" rubber yield data in even better accord with those from stretched fresh rubber than do those of Ott.[6]

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The Constitution of Inorganic Rubber

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There is a complete series of phosphonitrile chlorides of the general formula, $(PNCl_2)_x$, of which $(PNCl_2)_3$, $(PNCl_2)_4$, $(PNCl_2)_5$, $(PNCl_2)_6$, and $(PNCl_2)_7$ are already known.[1] All these compounds have the remarkable property of changing rapidly around 350° C. into an amorphous substance which is insoluble and infusible, and whose mechanical properties are similar to those of rubber. It is, for this reason, generally known as *inorganic rubber*. According to the various authors who have studied this substance,[2] the latter is a mixture composed solely of phosphonitrile chlorides of very high molecular weights.

In the present paper, it will be shown that, contrary to this hypothesis, inorganic rubber, like all the gums obtained by Renaud[3] at low temperatures, must contain, besides highly polymerized compounds which form a sort of network, lower members of the series which are confined in the meshes of this network. This assumption makes possible a simple interpretation of all the apparent phenomena of depolymerization of inorganic rubber which have been described up to the present time.

In accordance with the current nomenclature of polystyrenes, all the soluble phosphonitrile chlorides will be classed as α compounds, and the insoluble high polymers as β compounds. This notation serves to show the close analogy which exists between the organic series of polystyrenes and the inorganic series of phosphonitrile chlorides. In particular, it would appear that the β compounds of the two series resemble closely each other in their structures, *e. g.*, inorganic rubber shows, after being stretched, an x-ray fiber diagram.[4]

At ordinary temperatures, inorganic rubber loses gradually its elastic properties, and at the same time a crystalline structure appears within the mass. The crystallized part of the product dissolves slowly in organic solvents such as ether, dioxan, and hydrocarbons of the benzene series, with formation of solutions which contain preponderantly the trimeric and tetrameric chlorides of phosphonitrile. It may therefore be assumed, as Meyer, Lotmar, and Pankov have recently done,[4] that inorganic rubber depolymerizes slowly. However, this interpretation is open to certain objections, first of all because of the fact that inorganic rubber never crystallizes completely, and the part which remains amorphous and insoluble can be kept without alteration for years. Then again inorganic rubber in which crystalline forms have appeared regains its amorphous appearance and its elastic properties when it is heated at slightly elevated temperatures (50° to 90° C.), which correspond exactly to the melting point of the mixture of soluble polymers. When it is again let stand at room temperature, it recrystallizes only partially and only after several weeks.

Inorganic rubber behaves therefore as a mixture, part of which is soluble and crystallizes slowly, while the remainder is insoluble and cannot be crystallized. There appears then to be no good reason for assuming any depolymerization whatever of phosphonitrile chlorides at low temperatures.

When heated in water for some minutes, inorganic rubber is transformed into a product from which phosphonitrile chlorides of low molecular weights can easily be

extracted. On the other hand, in view of the known fact that the trimer and tetramer are still but slightly attacked when the higher members are already hydrolyzed completely into polymetaphosphimic acids, without the substitution of chlorine atoms by hydroxyl groups involving depolymerization, it can be concluded that the phosphonitrile chlorides recovered after decomposition of inorganic rubber are present in the original substance.

When inorganic rubber is heated slowly to 500° C., it is transformed into a black product which is both insoluble and infusible, and which is devoid of all elastic properties. This substance, which will be designated γ, appears to be the product of a general and complete polymerization of all the components of the inorganic rubber. If on the contrary the heating is more severe, only a relatively insignificant residue of γ-product is obtained; the greater part of the inorganic rubber distills and is recovered as a mixture of α polymers. This, however, does not involve depolymerization, as believed by Stokes,[1] but rather a volatilization of the greater part of the α-components of the original inorganic rubber before they have had time to become transformed into non-volatile β-compounds.

In the present state of the researches of the present author, the γ compounds appear to be the final members of the depolymerization of phosphonitrile chlorides. Below 500° C., phosphonitrile chlorides change progressively into more and more highly polymerized forms, and inorganic rubber, an ill-defined mixture of α- and β-compounds of widely differing properties, represents only one step in this progressive change. The γ-polymers seem then to be the only stable members at low temperatures, and obviously we owe our knowledge of all the other members only to the fortunate fact that their rates of transformation are relatively slow over a particularly wide temperature range.

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Chlorination of Polymers of Chloroprene Rubber

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The properties of chlorinated rubber lacquers prompted the authors to undertake a study of the optimum conditions of chlorination of chloroprene rubber as well as the properties of chlorinated polychloroprenes. To this end, a series of experiments on the chlorination of various polymers of chloroprene rubber was carried out. The difficulties of further addition of chlorine to polychloroprene were overcome by suitable conditions of chlorination.

Various polymers of chloroprene were chlorinated in the following manner.

CHLORINATION OF α-POLYMER OF CHLOROPRENE

Chloroprene was redistilled in a flask fitted with a fractionation column. The fraction boiling at 28.2° C. and 250 mm. pressure (mercury column) was dried over metallic sodium and then repeatedly fractionated in nitrogen. The distillation product was allowed to polymerize in nitrogen in darkness at room temperature (16–19° C.).

Preliminary analysis of this chloroprene showed the following constants: n_D^{20} 1.4582; d_{20}^{20} 0.9552; total chlorine by the Carius method, 40.32 per cent. The corresponding theoretical constants are: n_D^{20} 1.4583; d_{20}^{20} 0.9583; total chlorine (Carius), 40.08 per cent.

After eight days at room temperature the polymerization was equal to 17.32 per cent, at which point it was discontinued.

The percentage polymerization was determined by the conventional method, *i. e.*, a weighed sample of the polymerizate (4.0814 grams) was treated with alcohol and the precipitated polymer was dried in a thermostat to a constant weight (0.7068 gram).

A sample of 11 grams of polymerized chloroprene was used for chlorination. This polymer was precipitated from the sample with absolute alcohol and then purified by dissolving three times in chloroform (dried, redistilled, and tested for the absence of hydrogen chloride) and precipitating from the solution by absolute ethyl alcohol. The purified rubber was used in the preparation of a 1 *N* solution in chloroform. At the same time a 1 *N* chlorine solution in chloroform was prepared by conducting dry chlorine through chloroform.

The solution of chloroprene polymer was introduced into the solution of chlorine in chloroform cooled by ice. The chlorine solution was used in threefold excess, based on two chlorine atoms for each molecule of chloroprene.

The reaction mixture was let stand in darkness for 46 hours, and then was treated with absolute ethyl alcohol. The white viscous and partly flocculent precipitate, after three solutions in chloroform and precipitation with absolute alcohol, assumed a more brittle and pulverulent structure.

Drying in a vacuum desiccator to a constant weight transformed the product into a white powder with a yellow tint.

Analysis of this product gave the following results: 0.1578 gram of sample gave

0.401 gram of AgCl, or 62.8 per cent of total chlorine; calculated 66.2 per cent chlorine for the addition of two chlorine atoms.

Saponifiable Chlorine

The product was saponified in 0.1 *N* alcoholic sodium hydroxide, and the unaltered alkali was titrated with 0.1 *N* hydrogen chloride with thymolphthalein as indicator. Ten per cent of chlorine was saponified after two hours of treatment, and 15.5–15.8 per cent after four hours.

Temperature of Decomposition

Heating the product to 110° C. brought about no change; at 110–115° C. disintegration began with a yellow discoloration, and at 140–145° C. complete decomposition took place.

For the next experiment a chloroprene prepared and purified as in the first test was used.

After five days polymerization reached 17.9 per cent. A sample of 16 grams, containing 2.8 grams of polymer, was used in the chlorination.

The polymer was precipitated and purified as in the first experiment, and then used in the preparation of a 0.1 *N* solution in chloroform. This was introduced into an ice-cold 2 *N* solution of chlorine in chloroform in fourfold excess of the amount required theoretically for the addition of two chlorine atoms to each of the chloroprene links in the polymer. After standing in darkness for 48 hours, the mixture was treated with absolute ethyl alcohol. The snow-white precipitate, after purification by dissolving three times in chloroform and precipitating with alcohol, formed a hard and brittle powder. A solution of this polymer gave a white film after evaporation of solvent. In thin layers this film was transparent and highly brittle.

The chlorinated rubber was repeatedly washed with alcohol, and was then dried in a vacuum desiccator to a constant weight. The resulting chlorine derivative was a white powder. Analysis of 0.114 gram of the sample gave 0.3229 gram of AgCl, or 70.1 per cent total chlorine.

The addition of two atoms of chlorine gives a calculated chlorine content in the polymer of 66.8 per cent, and for that obtained by addition of two chlorine atoms and substitution of one hydrogen atom 72 per cent. Evidently the resulting chloride was a mixture of addition and substitution products.

After treatment of the polymer with alcoholic alkali by the previous method for four hours, 10.1 per cent of chlorine was saponified. When heated, the product changed from light yellow to dark yellow at 205° C., to dark red at 220° C., to black at 245° C., and finally carbonized at 255–260° C.

CHLORINATION OF *m*-POLYMER

The chlorination of the *m*-polymer of chloroprene was of considerable interest because of the insolubility of this polymer. In the chlorination of *m*-polymer, essentially the same experimental conditions were used as in the experiments with α-polymer.

m-Polymer was obtained by 100 per cent polymerization of chloroprene for three to four months, with exclusion of air. A sample of 2.4 grams was cut into small fragments and allowed to swell in chloroform for three days (0.1 *N* mixture). At the same time a solution of 2 *N* chlorine in chloroform was prepared (the total amount of chlorine was 4.5 times greater than theoretically required for the addi-

tion reaction). The chlorine solution was cooled with a freezing mixture and then added to the swollen *m*-polymer in chloroform. The mixture was kept in darkness. With progressing chlorination, the polymer passed into solution. Nearly five days were required to effect complete solution. The solution was filtered from some undissolved fibers, and the filtrate was treated with absolute grain alcohol. The precipitated product was filtered and purified by the method used in the preparation of α-polymer of chloroprene as described above. It was dried in a vacuum desiccator to a constant weight, forming a white powder.

Analysis of a 0.1142-gram sample gave 0.3116 gram of AgCl, or 67.5 per cent of total chlorine. Thus the product approaches the dichloride (calculated 66.8 per cent chlorine for dichloride and 72 per cent for trichloride).

The saponifiable chlorine was determined by heating the product in 1.5 *N* alcoholic sodium hydroxide.

Various results were obtained, depending on the duration of saponification: after 4 hours 13.5 per cent, after 12 hours 26.6 per cent, after 18 hours 32 per cent, and after 30 hours 39.8 per cent.

When heated, the product turned yellow at 132° C., bright yellow at 160° C., brown at 180° C., dark brown at 215° C., and completely carbonized at 250° C.

The films obtained from one of the products of chlorination of *m*-polymer were white, brittle, and had a high resistance to various concentrated acids. These films were tested with strong sulfuric and nitric acids, aqua regia, and 50 per cent sodium hydroxide. The films showed no change after eight days' contact. After 30 minutes in boiling nitric acid and aqua regia, there was no change in the films; in boiling sulfuric acid for 30 minutes the films underwent carbonization, whereas at 100° C. they remained intact; when heated in alkali they completely disintegrated.

Preliminary experiments on the chlorination of γ-polymer of chloroprene were carried out. The latter, as is well known, is characterized by a highly complex structure, which is explained by the presence of very frequent bonds between the chains. This polymer is very stable to the action of various solvents, in which it does not even swell after long periods. The action of chlorine solutions under the conditions previously described produced no changes in the γ-polymer. It changed but little, even on conducting chlorine into a suspension of the polymer in boiling chloroform.

Conclusions

Products of the chlorination of α- and *m*-polymers of chloroprene were obtained. The chlorine content of the chlorinated polychloroprene depended on the conditions of chlorination, but corresponded to products formed by the addition of chlorine. A large excess and high concentration of chlorine resulted in the addition of chlorine to the double bonds, together with partial substitution of hydrogen by chlorine.

Of the three basic types of chloroprene polymers, the α-polymer added chlorine most easily; *m*-polymer was chlorinated with more difficulty, giving a chlorination product of the composition, corresponding by analysis to the addition of chlorine at the double bond.

All polymers of chloroprene chlorinated under these conditions contained saponifiable chlorine.

Films of chlorinated polymers of chloroprene are characterized by a considerable stability to the action of various acids (nitric and sulfuric acids and aqua regia) in the cold and at moderately high temperatures.

γ-Polymer of chloroprene is not chlorinated under the same conditions.

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The Vulcanization of Rubber by Diazoamino Compounds

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Vulcanizing agents for rubber can be classified in the following six types:

(1) Sulfur, including α-sulfur, β-sulfur, γ-sulfur, precipitated sulfur, and nascent δ-sulfur.

(2) compounds containing sulfur, *e. g.*, sulfur chloride, sulfur iodide, sulfur dioxide, phosphorous sulfides, hydrogen persulfides, nitrogen sulfide, and alkaline polysulfides.

(3) elements of the sulfur group and their compounds, *e. g.*, selenium, tellurium, selenium sulfur chloride, and selenium diethyldithiocarbamate.

(4) halogens and halogenated compounds, *e. g.*, chlorine, bromine, iodine, hypochlorous acid, hypochlorites, and benzoquinone dichloride.

(5) oxygenated compounds capable of liberating nascent oxygen at vulcanizing temperatures, *e. g.*, persulfates (such as ammonium persulfate), peracids (such as perbenzoic acid), nitro compounds (such as 1,3,5-trinitrobenzene, tetranitronaphthalene, and nitrocyclohexane in the presence of metallic oxides), and organic peroxides (such as benzoyl peroxide).

(6) derivatives of rubber, *e. g.*, rubber ozonide, chlorinated rubber, brominated rubber, and rubber hydrochloride.

Among the compounds listed above the only ones which bring about vulcanization at room temperature are sulfur chloride, nascent sulfur (from the reaction of sulfur dioxide and hydrogen sulfide), sulfur dioxide, hydrogen persulfides, halogens, and hypochlorous acid. The most energetic and the most rapid of these is sulfur chloride.

The compounds which effect vulcanization at room temperature, and also those which are effective only at elevated temperatures, are sulfurated, oxygenated, or halogenated compounds, *i. e.*, those which contain elements capable of uniting with rubber. This is evident by the fact that rubber derivatives formed by these elements are known, *e. g.*, rubber disulfide, rubber ozonide, and halogenated rubbers.

With regard to vulcanization by compounds which contain nitrogen but no sulfur, Buizov[1] has called attention to the fact that rubber can be vulcanized by diazoaminobenzene. Buizov in his publication considers this observation to be of no particular importance, and it has been entirely ignored, in fact has not been mentioned in the literature on rubber since that time.

Independently of this discovery by Buizov, the present author has recently found that diazoaminobenzene, and particularly its homologs, *e. g.*, diazoamino-*p*-toluene, are energetic vulcanizing agents. Actually all diazoamino compounds of the general formula: $R—N{:}N.N\begin{matrix}X\\R'\end{matrix}$ (where R is an aryl group, R′ is an aryl, aralkyl, or arylamino group and X is hydrogen, a metal, or an alkyl, acyl, aryl, or aralkyl group) have been found to be vulcanizing agents.

If, on the other hand, R′ is an alkyl group and X is hydrogen or an alkyl group, the particular diazoamino derivative is not an active vulcanizing agent. This is

evident from the following table, which gives the diazoamino compound and its activity as a vulcanizing agent.

Compound	Vulcanizing Power
(1) Phenyldiazoaminobenzene $C_6H_5N : NNHC_6H_5$	Five per cent gives a good vulcanizate in 5 minutes at 143° C.
(2) Sodium salt of phenyldiazoaminobenzene $C_6H_5N : NNNaC_6H_5$	Extremely feeble vulcanizing power[2]
(3) Silver salt of phenyldiazoaminobenzene	Five per cent gives a good vulcanizate in 5 minutes at 143° C.
(4) Cupric salt of phenyldiazoaminobenzene $C_6H_5N : NNC_6H_5$ | Cu | $C_6H_5N : NNC_6H_5$	Five per cent has no vulcanizing action
(5) *p*-Tolyldiazoamino-*p*-toluene p-$H_3CC_6H_4N : NNHC_6H_4CH_3$-$p$	Two per cent gives a good vulcanizate in 5 minutes at 143° C. or in 30 minutes at 100° C., *i. e.*, it is more powerful than phenyldiazoaminobenzene
(6) Benzyldiazoaminobenzene $C_6H_5N : NN(CH_2C_6H_5)C_6H_5$	Five per cent gives a good vulcanizate in 5 minutes at 143° C.
(7) Benzyldiazoamino-*p*-toluene p-$H_3CC_6H_4N : NN(CH_2C_6H_5)C_6H_4CH_3$-$p$	Five per cent gives a good vulcanizate in 5 minutes at 143° C.
(8) Benzoyldiazoaminobenzene $C_6H_5N : NN(COC_6H_5)C_6H_5$	Two per cent gives a good vulcanizate in 5 minutes at 143° C.
(9) Benzoyldiazodiphenylurea $C_6H_5N : NN(CONHC_6H_5)C_6H_5$	Five per cent gives a good vulcanizate in 5 minutes at 143° C.
(10) Diazobenzenediphenylhydrazide $C_6H_5 : NN(C_6H_5)NH_2$	One per cent gives an optimum cure in 5 minutes at 143° C.
(11) Benzoyldiazopiperide $C_6H_5N : NNC_5H_{10}$	Very feeble vulcanizing power
(12) *p*-Toluenediazopiperide p-$H_3CC_6H_4N : NNC_5H_{10}$	Very feeble vulcanizing power
(13) Benzoyldiazodimethylamine $C_6H_5N : NN(CH_3)_2$	No vulcanizing power
(14) Benzenediazoethylamine $C_6H_5N : NNHC_2H_5$	No vulcanizing power
(15) Benzenediazodipropylamine $C_6H_5N : NN(C_3H_7)_2$	No vulcanizing power
(16) *p,p'*-Dinitrodiazoaminobenzene p-$O_2NC_6H_4N : NNHC_6H_4NO_2$-$p$	No vulcanizing power

It is already known[3] that, when heated, phenyldiazoaminobenzene evolves as free nitrogen two-thirds of its total nitrogen, with the formation of *o*- and *p*-aminobiphenyl, according to the reaction: $C_6H_5N:NNHC_6H_5 \longrightarrow C_6H_5C_6H_4NH_2 + N_2$.

The present author has found that this decomposition is very violent, though the dry compound does not explode when heated *in vitro* to 150° C., either in a current of inert gas or in a current of moist air.

Now compound (2) in the list above decomposes *in vitro* only to a very slight extent at 150° C., either in a current of nitrogen or in moist air; compound (4) does not decompose at all under the same conditions; compounds (1), (3), (5), (6), (7), (8), (9), and (10) decompose with great violence *in vitro* in much the same way that phenyldiazoaminobenzene does between 140° and 160° C., with evolution of nas-

cent nitrogen. On the other hand, compounds (11) to (16), which have little or no vulcanizing activity, do not decompose *in vitro* even at 200° C.

It is evident therefore that the only diazoamino compounds which are active vulcanizing agents are those which decompose with evolution of nascent nitrogen at temperatures close to vulcanizing temperatures.

The necessity of the third (imino) nitrogen atom being united directly to the diazo group to obtain any vulcanizing power seems to be demonstrated by the fact that diazonium salts of the R—N: N—Xtype, where X is chlorine or an acyl group, are not vulcanizing agents, though they are, like numerous other diazoamino compounds, rather unstable compounds which evolve nitrogen when they decompose. For example, diazobenzene chloride, diazo-*p*-toluene chloride, benzoyldiazobenzene; and diazobenzeneethyl xanthate have no vulcanizing activity, though it is possible to add them to rubber without any decomposition during mixing operations.

As is to be expected, azo compounds and azoamino compounds of the respective formulas: RN: NR and RN: $NC_6H_4NH_2$, *e. g.*, azobenzene and *p*-aminoazobenzene, are devoid of any vulcanizing activity, since none of these compounds contains a loosely combined diazo group.

In so far as the mechanism of the action of diazoamino compounds in vulcanization is concerned, it is probable that they function essentially as polymerizing agents since they are likewise energetic polymerizing agents of diolefins.

The results described in the present paper are therefore in favor of the theory that vulcanization is a result, at least in part, of polymerization; in fact the work described represents the chief experimental contribution up to the present time which may be considered to be in favor of this theory.

As for the characteristics of rubber products vulcanized by diazoamino compounds, it should be remarked that such mixtures should be vulcanized in the absence of air, *e. g.*, in a mold in a press, in order to avoid stickiness. This tendency towards stickiness is similar to that of rubber vulcanized with benzoyl peroxide, which is an energetic vulcanizing agent of about the same effectiveness as are some of the diazoamino compounds.

Though having good physical properties and a particularly high resistance to solvents, such as benzene and benzine, the products obtained by vulcanization with diazoamino compounds have a tendency to be porous, and when prepared from natural rubber, age poorly and become sticky. On the other hand, when prepared from synthetic rubber, they age in a normal manner, and there is no tendency to become porous during vulcanization.

Attempts to extend the work to the vulcanization of latex by diazoamino compounds have so far been unsuccessful, because of the low solubility in water of the compounds tested. Likewise attempts to vulcanize oils by diazoamino compounds have been fruitless.

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[2] This inactivity probably depends on the fact that, when mixed into rubber, this salt is decomposed by traces of moisture into diazoaminobenzene and sodium hydroxide; in fact a rubber mixture containing diazoaminobenzene and sodium hydroxide in the stoichiometric proportions corresponding to the sodium salt above behaves like the sodium salt itself, *i. e.*, is a feeble vulcanizing agent.

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Purified Rubber for Electrical Insulation

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THE water absorption and the dielectric stability of soft rubber insulating compounds under wet conditions is influenced by the kind of crude rubber employed. For most rubber-covered aerial and building wire where moisture conditions are not severe, the better grades of plantation rubber are satisfactory. However, for service involving immersion for long periods in fresh water, a need exists for rubber containing less nonhydrocarbon water-absorbing substances than the plantation product. This is particularly true when the insulating wall is thin and a high degree of electrical stability is required.

Only recently has the preparation of such a type of purified rubber been given serious consideration on the plantations in the Far East. In the past, coöperation on such a problem with the plantation has been difficult, and for that and other reasons methods have been developed here for preparing this rubber in the factory. The purpose of this paper is to discuss the nature and role of protein and other substances found in Hevea rubber and to outline various methods for purifying rubber. Data are presented on the composition and properties of the resulting products.

Composition of Latex and Sheet Rubber

Hevea latex consists essentially of a watery serum in which round and pear-shaped rubber particles are colloidally dispersed and exhibit Brownian movement. According to the literature, these negatively charged particles vary from about 0.5 to 3μ in diameter, and some have tails varying in length up to 5μ. Langland (*22*) recently determined that there are about 0.6×10^{12} rubber particles in 1 cc. of latex containing 38.5 per cent solids. That this figure is probably too low is indicated by the fact that a large number of particles exist which are so small as to be beyond the resolving power of the microscope used by Langland. The particles are believed to have an adsorbed film of protein on their surface and to contain some fatty acid and sterol complexes (lipids) either as a part of the adsorbed layer or associated with the rubber hydrocarbon making up the particle. As is shown later, only about 10 per cent of the total nonhydrocarbon solids appear to be associated with the latex particles. A more or less typical analysis of a fresh lot of normal ammonia-preserved latex is as follows:

	% Based on: Latex	% Based on: Dry solids
Total solids	40.02	...
Water and ammonia	59.98	...
Acetone ext.	2.05	5.12
Water-sol. substances[a]	3.04	7.59
Ash	0.42	1.05
Nitrogen	0.24	0.61
Rubber hydrocarbon[b]	33.98	84.90
Nonrubber hydrocarbon substances	6.04	15.10

[a] Method of Fowler (*18*).
[b] Method of Kemp (*16*). The iodine value was determined on acetone-extracted solids after passing them several times through tight mill rolls to render them soluble in CS_2.

The literature reveals more than fifty different nonhydrocarbon substances in latex, some in only minute amounts. The main constituents are the proteins, fatty acids, sterol and sterol complexes, quebrachite, carbohydrates, and the so-called water-soluble salts. The ash of dried latex is composed principally of P_2O_5 and the alkaline earth oxides which appear for the most part to be chemically combined with organic substances in the latex, forming complex salts. The substances found in latex are of the types generally associated with living matter. Many of these substances are very complex and undergo changes upon exposure to air which make their identification difficult. Undoubtedly there are important substances in latex which have not yet been identified. For example, Roberts (*27*) only recently obtained evidence of a complex sulfur compound present in latex to the extent of 0.92 per cent (2.4 per cent on solids).

In the coagulation of diluted latex on the plantation with formic or acetic acid, followed by washing to make sheet rubber, a large proportion of the water-soluble serum substances is removed. The extent of this purification is indicated from the increase in the rubber hydrocarbon content from about 85 per cent in dried latex to 92–95 per cent in sheet rubber. It is well known, however, that plantation smoked sheets retain a considerable quantity of water-soluble serum solids, whereas the soluble substances of crepe are generally more completely removed by the added washing it receives at the plantation.

Effect of Washing Sheet Rubber

The importance of employing rubber and compounding ingredients free from water-soluble impurities in the manufacture of submarine cable insulation has been the subject of several publications (*35*) by these laboratories. As a result of early work in this field, thoroughly washed plantation smoked sheet rubber was first commercially employed in the manufacture of the San Pedro–Catalina Island telephone cables (*13*) laid in May, 1923. In order to make accurate tests on this type of insulation under sea bottom conditions, a 2-mile length of cable was sealed at one end and laid in deep water off Avalon Harbor at the time the regular cables were laid. Electrical measurements have been made periodically on this cable, and the results are as follows:

	Tests after Laying in May, 1923	Tests in March, 1935
D. C. capacitance, microfarad/nautical mile	0.277	0.289
A. C. capacitance (30 cycles), microfarad/nautical mile	0.268	0.274
A. C. conductance (30 cycles), mho/nautical mile	0.36	0.24
D. C. insulation resistance, megohms/nautical mile	14,000	29,000
Dielectric constant	3.21	3.28
Power factor (30 cycles), %	0.71	0.47

The rubber used in the Catalina Island cables was washed 5 hours in a Werner and Pfleiderer internal-type washer. This kind of rubber requires only a short period to become plastic on the mill and vulcanizes satisfactorily. For example, a compound of 85 per cent rubber, 5 per cent sulfur, 5 per cent zinc oxide, and 5 per cent litharge had a tensile strength of over 215 kg. per sq. cm. when vulcanized 1 hour at 142° C. Although it has been the practice of cable manufacturers to wash Up-River fine Para and other wild rubber for short periods to remove bark and other adventitious impurities, the washing of the better plantation grades is not required for many types of wire and therefore has not been the general practice, notwithstanding a recent statement by Boggs and Blake (*9*) to the contrary.

Boggs and Blake recently stated (*9*) that in 1924 they discovered that water absorption in rubber is caused principally by the proteins naturally present. Data were presented purporting to show that the proteins contributed more to water absorption of crude rubber than do the water-soluble impurities removable by washing. Their method (*8*) of determining water absorption involves immersing a sheet of rubber 0.073 inch (1.85 mm.) thick in distilled water at 70° C. for 20 hours. The present author finds this procedure not well suited to show the wide differences which exist in the water absorption of various types of rubber. The differences in the water absorption of purified and nonpurified rubber brought out in such a short period are much less than those which are shown after long periods of soaking. Since the ultimate purpose of the rubber is to furnish insulation on cables which may be immersed in water for years, it is obvious that something more than a 20-hour period of immersion should be employed in evaluating the rubber. Although many data on the effect of washing on water absorption of smoked sheet and other crude rubber have already been published by these laboratories (*23*, *35*), additional data obtained after long periods of immersion are plotted in Figure 1 to show that the presence of water-soluble substances are responsible for most of the water absorption of plantation smoked sheet.

The lower water absorption of crepe rubber is due to the more effective washing given it on the plantation. If the latex is diluted more before coagulation to make crepe, the water absorption is further reduced. Although the nitrogen content in this particular case is higher than usual, the ash content is only 0.07 per cent, indicating a more complete removal of water-soluble salts than is usual for crepes, the ash content of

which is generally about 0.2 per cent. Even under the best washing conditions, however, it is difficult to remove the last traces of water-soluble matter from plantation sheet rubber.

There appears to be no definite relation between the protein content of rubber and the water absorption except that, as proteins are removed, the removal of water-soluble substances

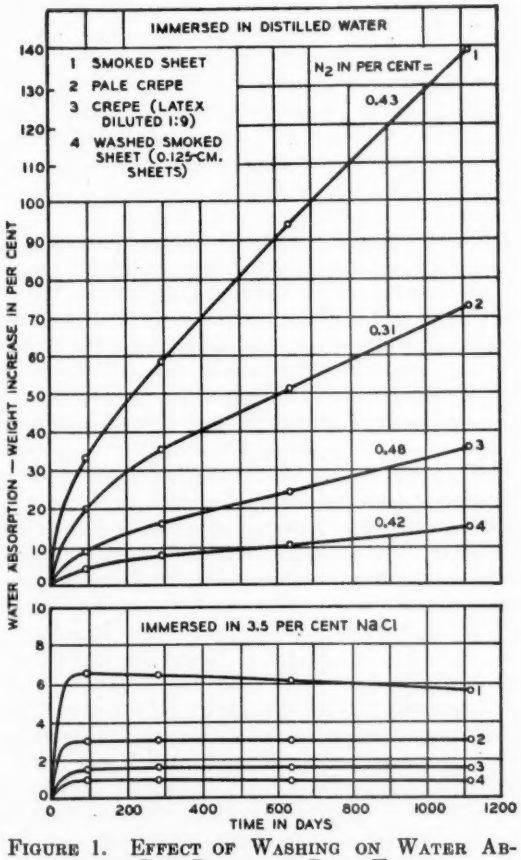

FIGURE 1. EFFECT OF WASHING ON WATER ABSORPTION OF RAW RUBBER AT ROOM TEMPERATURE

is usually more complete. The Boggs and Blake method was used to determine the water absorption of various types of rubber before and after washing and deproteinizing. The results obtained are given in Table I. A recent patent (7) refers to tests on the effectiveness of deproteinization made by limiting the water absorption by the Boggs and Blake method to 10 mg. per square inch as a maximum. This limit can be reached by washing, and even deproteinized rubber may or may not meet this requirement. Caucho ball rubber from the

species Castilla fails to meet this limit, but from its nitrogen content it would be considered deproteinized rubber. It is apparent that proteins are not the controlling factor in the absorption of water. Water absorption data given by Boggs and Blake (*9*) before and after washing plantation crepe rubber 4 hours show a reduction of only 10 per cent in the water absorption as a result of washing. The results given in Table I indicate a 40 per cent reduction in the water absorption of a sample pale crepe when it is washed only 2 hours. It is known, of course, that different lots of pale crepe vary considerably in water absorption.

The reason why water-soluble impurities are more effective than proteins in causing water absorption is readily explained on the basis of the osmotic mechanism for water absorption proposed by Williams and Kemp and discussed in several publications and patents (*35*). That osmosis is all important in water absorption is supported by an overwhelming mass of evidence. Even an extremely small amount of soluble crystalloids of low molecular weight causes extensive osmotic swelling of raw rubber in distilled water, since the lower vapor pressure over the solution of these salts within the rubber sets up a pressure gradient to the outside water. Water is slowly drawn into these internal solutions which tend to become diluted to an infinite degree or until the osmotic swelling pressure is overcome by the resistance of the rubber itself to swelling. In the case of the more rigid, tougher, vulcanized rubber, the end point is reached before infinite dilution occurs. The resistance to swelling of ebonite, for example, is so great that osmotic action is largely prevented. When the rubber is immersed in salt solutions, sorption stops when the vapor pressure of the internal solution equals that of the outer solution. Most proteins possess extremely high molecular weights; since those in plantation Hevea sheet rubber are not water soluble,[1] it is obvious that their effect is relatively small in comparison with solutes which are not diffusible through the rubber membrane. This osmotic mechanism explains why crude rubber continues to absorb water and swell over extremely long periods upon immersion in distilled water. It also explains why the water absorption of rubber reaches an early equilibrium in sea water and stronger salt solutions in which it absorbs much less water than in distilled water.

Nature of Proteins

Numerous investigations have been made to determine the nature of protein in Hevea latex. Although the exact nature of this protein is still unknown, much has been learned concerning it. All of the protein and other nitrogenous bodies in latex appear to be present in the serum except for a small amount which is apparently adsorbed strongly on the surface

[1] Boggs and Blake (*8*) found that the protein separated from smoked sheet was nonhygroscopic when exposed to atmospheric moisture.

TABLE I. WATER ABSORPTION AND NITROGEN CONTENT OF WASHED AND UNWASHED CRUDE RUBBER BY BOGGS AND BLAKE METHOD

Rubber	Per Cent N_2 on Dry Basis	Mg. of Water Absorption for 20 Hr. at 70° C. Per sq. in. of surface	Per sq. cm. of surface
Hopkinson sprayed rubber	0.53	..	...
Hopkinson sprayed rubber, washed 2 hr.	0.32	27	4.2
Pale crepe	0.31	17	2.6
Pale crepe, washed 2 hr.	0.30	10	1.6
Crepe (laboratory):[a]			
First lot	0.29	9.4	1.5
Second lot	0.29	7.5	1.2
Caucho ball (Castilla)	0.24	..	...
Caucho ball, washed 2 hr.	0.06	13	2.0
Deproteinized Hevea	0.03	9.4	1.5
Deproteinized Hevea	0.09	5.4	0.8
Pale crepe, different lots	..	12–22	1.9–3.4

[a] Normal ammonia-preserved latex diluted 1 to 3 volumes with water, coagulated with 1 per cent acetic acid, and washed on creping rolls.

of the particles. Whether the adsorbed protein is the same as the serum protein is not known. Some investigators consider that the protein exists as a complex compound with fatty acid or other constituents of the serum. Spence (*31*) considered it to be a glycoprotein. Some evidence exists that the protein is in complex combinations either with fatty acids or phosphoric acid, both of which are present in considerable quantities in the serum. Evidence at hand indicates that about half of the nitrogen in Hevea latex is present in an acid-coagulable protein and that the remaining nitrogenous substances are soluble in dilute acids. Some amino acids and peptones are known to be present in latex, but the composition and nature of these soluble nitrogenous bodies are not well defined.

Removal of Nitrogenous Matter

As seen in Table I, nearly 40 per cent of the nitrogen content of Hopkinson's sprayed rubber is removed by washing in water; its final nitrogen content is about the same as that of first-quality crepe. In the acid coagulation of latex followed by washing to make crepe, Eaton and Day (*11*) found that 38.5 per cent of the nitrogen-containing bodies had been removed. De Vries (*32, 33*) found the nitrogen content of a fresh dried film of latex had decreased from 0.67 to 0.37 by extracting it with water, this water extract amounting to 5.7 per cent of the dried latex.

According to Boggs and Blake (*8*), sprayed rubber has a 20-hour water absorption of 200 mg. per square inch. Referring to the author's value of 27 mg. per square inch for washed sprayed rubber, it is seen that the presence of water-soluble substances has a profound effect on water absorption.

Schidrowitz and Kaye (*29*) found that about 80 per cent of the proteins can be removed from Castilla rubber by washing; this result is confirmed by experiments made in these labora-

tories. It is interesting to note that the nitrogenous matter in Surinam sheet balata is largely removed by washing. In the crude state this balata contains about 0.7 per cent nitrogen which is reduced to about 0.05 per cent upon washing. The soluble nitrogenous fraction in balata differs widely from protein in composition although it gives protein reactions (*5*).

Boggs and Blake (*9*) contend that proteins cannot be removed from rubber by simple washing. This statement needs qualification since the proportion of nitrogenous substances removed depends upon the type of rubber, the treatment of the rubber before washing, and the method of washing employed. Repeated creaming with a centrifuge or by the use of creaming agents is a simple washing procedure which results in the removal of a large portion of the proteins from Hevea latex serum.

Continuous Protein Phase in Crude Rubber

In the coagulation of latex with dilute acetic acid on the plantation to make sheet rubber, it appears that the rubber particles retain their adsorbed protein film upon flocculation, apparently coming together without bursting and flowing, and carrying down with them some precipitated protein and other serum substances which are entrapped between the particles (*1*). Evidence that this is the case was obtained by the author who showed by electrical means (*15*, *17*) that a continuous network of protein and water-soluble matter must exist between the rubber particles in smoked sheet to account for the rapid and complete electrical insulation failure through the sheet when it is immersed in water for a short period (Table III). These water-absorbing impurities rapidly become conducting, as soon as water diffuses into the rubber, and make continuous leakage paths for the electrical current. Sebrell, Park, and Martin (*30*) observed an opaque particle outline in thin films of dried latex which were subsequently immersed in water. Microscopic observations of latex particle flocculation were made in these laboratories, and it appears that these particles come together with extremely strong adhesion forces without bursting.

Nature of Adsorbed Layer on Rubber Particles

Although it is generally agreed that some sort of adsorbed layer exists on the surface of the latex particles, the exact nature of this layer is in doubt. That it does exist, however, is confirmed by a large amount of indirect experimental evidence. It has been postulated that this layer may contain fatty acid, protein, or protein complex, and a fatty acid–sterol complex. In a recent review, Kemp and Twiss (*21*) adduced from cataphoresis studies of latex that the rubber particles contained an adsorbed layer of protein and "resin" (acetone-soluble matter).

To obtain information on this point, several years ago P. A. Lasselle, under the author's direction, washed normal ammonia-preserved rubber latex by repeatedly creaming it in a laboratory centrifuge. Rubber was also prepared from the original latex used in this experiment as follows:

> The first cream was separated and diluted to three times its volume with 0.5 per cent ammonia and recreamed. This was repeated twice. Part of the rubber coagulated from the cream in the fourth separation. This was dried and analyzed. The remaining uncoagulated rubber was washed similarly three additional times with dilute ammonia and twice with distilled water. This final cream was extremely stable and did not coagulate spontaneously after several months of storage on a laboratory bench in an Erlenmeyer flask exposed to air. Some of the final cream after the last centrifuge treatment was diluted with distilled water to 7 per cent rubber content and coagulated with dilute acetic acid. Most of the rubber quickly coagulated, but even after several hours the serum contained some dispersed rubber.

The analysis of this rubber from the original latex and the products from the fourth and ninth creaming is shown in the following table; a large proportion of the smaller rubber particles from the original latex was lost in the process, being discarded with the skim so that the analysis represents the composition of the large particles only (as per cent of the dry rubber):

	Rubber from Original Latex	After Fourth Creaming	After Ninth Creaming
Nitrogen	0.322	0.067	0.056
Ash	0.203	0.004	None
Acetone ext.	3.05	2.45	1.48

It appears that there is adsorbed on the finally washed rubber particles an amount of ash-free protein corresponding to 0.35 per cent based on the dry rubber which cannot be removed except by vigorous treatment such, for example, as heating in the presence of strong sodium hydroxide solution. The freedom from ash and resistance to hydrolysis is evidence that this layer material is not lecithin. After acetone extraction this rubber had a 99.5 per cent rubber hydrocarbon content as determined by the author's iodine chloride method. Belgrave (*4*) obtained a value of 0.06 per cent nitrogen, corresponding to 0.38 per cent protein in rubber which he had coagulated by the addition of alcohol to latex that had been highly diluted with water, the rubber being washed before nitrogen was determined. There is the possibility that a heavier protein layer exists on the latex particles in their normal state, and the above figure represents the minimum amount that can exist—i. e., possibly a monomolecular layer.

The above data seem definitely to support the idea that rubber particles in latex have an adsorbed layer of protein and contain acetone-soluble matter (resin) which is either adsorbed or contained within the particle. Some ammonia-preserved rubber latex (39.2 per cent solids) was recently subjected to four creaming operations in one of the De Laval

special machines. Before the first creaming the latex was diluted 1 to 4 with 0.75 per cent ammonia. After each creaming the cream was diluted 1 to 4 with 0.75 per cent ammonia before the next creaming. The analysis of the rubber from each cream after drying is given in Table II.

TABLE II. EFFECT OF REPEATED CREAMING WITH DE LAVAL SEPARATOR

	First Cream	Second Cream	Third Cream	Fourth Cream
Solids, %	61.2	56.2	52.9	45.8
Nitrogen,[a] %	0.147	0.122	0.108	0.093
Ash,[a] %	0.19	0.10	0.06	0.04
Acetone ext.,[a] %	2.23	2.06	2.24	2.10

[a] On dry rubber basis.

The acetone extract from the dried rubber of the fourth separation had an acid value of 51 and saponification value of 103, in comparison with the acetone extract of (Rubber Cultuur Maapschappij Amsterdam) crepe with an acid value of 81 and a saponification value of 122. It is evident from these data that one or more fatty acids and what is probably a fatty acid–sterol complex (possibly phytosterin) is either adsorbed on or contained within the rubber particles. It has already been postulated by Beumée-Nieuwland (*6*) that such a fatty acid complex or lipoid film is adsorbed on the rubber particles. However, some evidence exists that part of the acetone-soluble matter may be contained within the rubber particle. We find, for example, that, upon heating latex in the presence of 1.0 per cent sodium hydroxide for 2 hours in an autoclave at 150° C., it is possible to reduce the nitrogen content to less than 0.02 per cent. However, after the treated latex was coagulated with acetone or alcohol, washed, and dried, the rubber still contained 1.29 per cent of acetone-soluble substances. The acid value of this residual resin ranged from 11 to 15 and the saponification value from 43 to 44. Unsaponifiable matter makes up a large proportion of these acetone-soluble substances. The difficulty of removing this residual resin is taken as evidence that at least some of it is contained within the particle. It is suggested that this portion may be phytosterol.

In the case of Surinam sheet balata, which contains about 40 per cent of a soft sticky resin, the indication is that much of this resin exists inside the particles, since balata sheet is not sticky as would be the case if the resin were outside the particles. Balata resin contains practically no free fatty acid and appears to be largely composed of sterols and sterol esters.

Methods for Purifying Rubber

Since water-soluble electrolytes and proteins are present on the surface of and between the rubber particles, they are in the worst possible position within the rubber as regards their effect on electrical properties when wet, making their removal

desirable when the maximum electrical stability of rubber insulation for use under wet conditions is required. Since proteins and water-soluble matter are intimately associated in the rubber, it is apparent that any process that removes protein will also remove the water-soluble constituents, a fact which is apparently lost sight of by Boggs and Blake (*9*) in crediting deproteinization for most of the reduction which they found in the water absorption of deproteinized rubber. On the other hand, the removal of water-soluble substances from plantation sheet rubber by washing is made difficult because of their close association with the dried protein which acts as a binder. Any method for purifying rubber to be suitable for commercial purposes must yield a product which is not too soft and will vulcanize and age satisfactorily.

Organic Solvents. The literature abounds with references to the separation of the "insoluble substances" from rubber dissolved in organic solvents. Several patents (*2*) disclose methods of this general type. A patent (*7*) issued as recently as 1935 gives this procedure as a means of preparing deproteinized rubber. These methods are obviously not well adapted to commercial use on account of the difficulty of handling the highly viscous rubber solutions in organic solvents and the sticky and soft nature of the product. It is also well known that the proteins are not always completely removed by this solvent method.

Centrifuge Washing. This method offers promise provided it can be carried out economically. It may be a rather costly procedure especially when the considerable portion of the rubber contained in the skim is not recovered. More than three separations are undesirable on account of the possible danger of coagulation and the increased cost. Rubber from three creamings has a nitrogen content of about 0.1 per cent and is low in ash content as shown in Table II. It vulcanizes satisfactorily if suitable accelerators are used. An antioxidant is usually added to this type of purified rubber to take the place of the natural antioxidants lost during purification. Most deproteinized rubber is softer and plasticizes more rapidly on the mill than sheet. The addition of a small amount of antioxidant makes it possible to control this process more accurately.

Creaming Agents. Irish moss, agar-agar, tragacanth, and similar agents will cream warm latex more effectively than the centrifuge without so much loss of rubber. Creaming with alginates was shown by McGavack (*24*) to produce a rubber suitable for insulation. The rubber produced by this process appears to be similar in composition and properties to that produced by the centrifuge method.

Creaming with Strong Alkali. De Vries and Beumée-Nieuwland (*34*) and later Pummerer and Pahl (*25*) found that most of the nitrogenous matter can be removed from latex by creaming it repeatedly by the addition of strong sodium hydroxide which is then washed out. Cummings and Se-

brell (*10*) employed a modification of this method and obtained rubber with a nitrogen content of less than 0.01 per cent. Although this process has value as a laboratory procedure, it appears to be unsuitable for commercial purposes on account of the difficulty of removing all the alkali. Rubber purified in this way oxidizes and perishes rapidly upon exposure to air.

USE OF ENZYMES. It has long been known that the natural enzymes present in latex or an added enzyme such as trypsin or papain will cause fairly rapid hydrolysis of the proteins when the pH and temperature of the latex are adjusted properly. About five years ago, rubber was purified by this method in these laboratories in coöperation with the Wallerstein Laboratories of New York. The crepe made from ammonia-preserved latex by this method appeared normal in properties and contained about 0.1 per cent nitrogen. Roberts (*26*) is studying this method in Malaya.

HYDROLYSIS METHODS DEPENDING ON HEAT. Several years ago the author (*18*) found that proteins in ordinary plantation sheet rubber which is immersed under water and heated in an autoclave at elevated temperature become hydrolyzed—i. e., break down to peptones or amino acids which can be subsequently washed out of the rubber. When water alone is used, this process requires an extended time or a high temperature, or both; these conditions are somewhat objectionable for factory operations, and the rubber is likely to be too soft. If strong ammonia is substituted for the water (*20*), a more rapid hydrolysis and solution of the proteins within the rubber result. A treatment of crepe immersed in concentrated ammonia for 2 or 3 hours at 115° C., followed by removal of the excess ammonia and washing, suffices to give a product with a nitrogen content of about 0.1 per cent and an acetone extract of about 2.1 per cent. Under the more severe treatment of a higher temperature or longer time, the nitrogen content has been reduced to 0.05 per cent and the acetone-soluble matter to 1.37 per cent. This rubber is excellent in quality and compares favorably with the best rubber produced by other methods.

Sandikov (*28*) found that proteins such as casein are broken down to peptones and amino acids by heating in ammonia. Several investigators, mentioned by Bedford and Winkelmann (*3*), have stated that crude rubber emulsifies when immersed in strong ammonia. The writer has not found this to be the case. Smoked sheet or crepe rubber does not emulsify when immersed in concentrated ammonia for 8 months at room temperature or as a result of the high-temperature treatment described. Unmilled smoked sheet placed in 28 per cent ammonia solution for 245 days at room temperature absorbed 19.2 per cent of the solution. During this period the solution was replaced with fresh ammonia five times. The total extracted matter was 1.88 per cent. Crepe given the same treatment absorbed 21 per cent ammonia and lost 0.96 per cent extracted matter. The extracted matter appeared to be com-

posed largely of soaps. The extracted smoked sheets after removing the ammonia were distinctly lighter in color.

Rubber latex can also be employed (*18*) in which case it is generally diluted with water, to which is added a small amount of ammonia or sodium hydroxide, and heated in stainless steel autoclaves under pressure for 2 or 3 hours at 150° C. This process can be carried out without coagulation of the rubber by employing a method already outlined (*19*). After cooling, the latex is further diluted with water, coagulated with dilute acetic acid, and washed in the regular manner. It is interesting from the scientific point of view that partial coagulation results on diluting this treated latex with water prior to adding acid, indicating that the latex particles tend to flocculate upon removal of the protein layer. This flocculation of particles from latex treated by the above process has been observed under the microscope. The rubber prepared by this method usually contains from about 0.02 to 0.04 per cent nitrogen.

TABLE III. EFFECT OF HEATING AND VULCANIZATION ON DIELECTRIC PROPERTIES AND WATER ABSORPTION OF SMOKED SHEET RUBBER

Sheet Thickness	Immersion Period	Water Absorption	Dielectric Constant[a]	Power Factor[a]	D. C. Resistivity
Cm.	*Days*	%		%	*Ohm-cm.*
Raw Unwashed Unmilled Smoked Sheets Immersed in 3.5% NaCl at Room Temp.					
0.42	0	0	2.34	0.14	2.2×10^{15}
	7	1.66	31.2	456	[c]
	14	2.44	[b]	[b]	[c]
	28	3.32	[b]	[b]	[c]
0.40	0	0	2.36	0.16	1.2×10^{15}
	7	2.20	[b]	[b]	[c]
	14	2.96	[b]	[b]	[c]
	28	3.92	[b]	[b]	[c]
Raw Unwashed Unmilled Smoked Sheets Heated 16 Hr. under Vacuum at 70° C., Then in Press, 1.5 Hr. at 142° C. in Mold; Sheets Immersed in 3.5% NaCl at Room Temp.					
0.33	0	0	2.56	0.19	1.0×10^{15}
	7	1.03	6.46	35.7	1.0×10^{10}
	14	1.34	8.25	38.9	3.5×10^{9}
	28	1.72	9.94	42.3	[c]
0.26	0	0	2.51	0.16	1.3×10^{15}
	7	1.27	4.31	15.9	4.4×10^{11}
	14	1.59	4.56	16.2	2.2×10^{11}
	28	1.96	4.80	16.6	3.5×10^{11}
Vulcanized Smoked Sheets[d] Immersed in Distilled Water at Room Temp.					
0.25	0	0	2.73	0.16	$>5 \times 10^{15}$
	7	1.10	3.08	0.28	$>5 \times 10^{15}$
	14	1.57	3.13	0.27	$>5 \times 10^{15}$
	28	2.08	3.17	0.31	$>5 \times 10^{15}$
0.25	0	0	2.72	0.18	$>5 \times 10^{15}$
	7	1.17	3.12	0.28	$>5 \times 10^{15}$
	14	1.66	3.15	0.21	$>5 \times 10^{15}$
	28	2.11	3.20	0.29	$>5 \times 10^{15}$

[a] Tests at 1000 cycles per second and room temperature.
[b] Values too high to measure accurately.
[c] Values too low to measure accurately.
[d] Composition (cured 90 min. at 126° C.):

European ribbed smoked sheets	100
Zinc oxide	3
Sulfur	3
Captax	0.5
Stearic acid	0.5

Effect of Vulcanization on Water Absorption and Dielectric Stability

The widespread difference between the water sorption and electrical stability of crude rubber, soft vulcanized rubber, and ebonite requires explanation. As shown in Table III, unmilled plantation smoked sheet rubber fails rapidly as an electrical insulating material when immersed in 3.5 per cent salt solution. Smoked sheets fail even more rapidly when immersed in distilled water. This rapid failure has been observed in smoked sheets from several sources and occurs even in first-quality European ribbed smoked sheets. If the sheets are heated in the press at 142° C. for 1.5 hours, the rubber absorbs less water and becomes electrically more stable. This is probably due to the heat hardening of the proteins. Milling tends to disperse the protein network, and sulfur probably reacts chemically with the protein. All three of these factors apparently aid in the stabilization of the dielectric properties of soft vulcanized rubber. The comparative stability of soft vulcanized rubber as compared with crude rubber is strikingly shown in Table III. Vulcanization also increases the resistance of rubber to swelling, thereby reducing the amount of water absorbed; this effect is at its peak in the case of ebonite which absorbs less than 0.5 per cent water when immersed 3 years in distilled water at room temperature, whereas raw rubber absorbs over 100 per cent water under the same conditions (Figure 1).

Vulcanizing and Aging Properties of Deproteinized Rubber

Boggs and Blake (*9*) indicated that the vulcanizing properties of deproteinized rubber are the same as plantation sheets. The author has not found this generally to be the case, although it must be kept in mind that deproteinized rubber prepared by different procedures may vulcanize differently. Boggs and Blake (*9*) failed to give details as to what kind of deproteinized rubber they were dealing with, as well as details as to the compositions studied. For example, it has been found that with certain accelerators deproteinized rubber does not cure satisfactorily and, with others, tensile strengths of well over 3000 pounds per square inch (211 kg. per sq. cm.) are obtained in pure gum stocks. In most cases the acceleration of the purified rubber must be increased to bring up the modulus to that of crepe or smoked sheets. A few data to show these effects are given in Table IV, using a deproteinized rubber made by treating crepe with strong ammonia (*20*).

This difference in vulcanizing properties between purified and plantation rubber can be explained on the basis that the acceleration due to amino acids, peptones, or other soluble nitrogenous substances in the plantation product is eliminated by removing these substances in the purification process.

TABLE IV. VULCANIZING PROPERTIES OF DEPROTEINIZED *vs.* PLANTATION RUBBER

	I	II	III	IV	V	VI
	Composition					
Pale crepe	100.0	....	100.0	....	100.0	....
Deproteinized (N_2, 0.09%)	....	100.0	....	100.0	....	100.0
Zinc oxide	3.0	3.0	3.0	3.0	3.0	3.0
Sulfur	3.5	3.5	2.5	2.5	2.5	2.5
Tetramethylthiuram monosulfide	....	....	0.5	0.5	0.4	0.4
Zinc dimethyl dithiocarbamate	....	....	....	....	0.1	0.1
Stearic acid	0.75	0.75	0.5	0.5	1.25	1.25
Aldehyde amine (808)	1.00	1.00	....	....	....	....
	Physical Properties					
Best cure at 142° C., min.	20	20	5	10	7	7
Tensile strength, kg./sq. cm.	242.6	112.5	226.7	175.0	237.8	226.7
Elongation at break, %	690	940	765	785	700	720
Load, kg./sq. cm.:						
At 500% elongation	66.8	10.5	33.4	24.6	58.0	29.9
At 600% elongation	144.1	21.1	73.8	42.2	126.5	87.9

The resistance of deproteinized rubber to accelerated aging appears to be satisfactory when suitable antioxidants are used. Crepe rubber purified by heating with strong ammonia solution has unusually good aging properties. For example, a pure gum stock which had an original tensile strength of 221.5 kg. per sq. cm. had a tensile of 235.5 kg. after aging 5 days under 3.5 kg. per sq. cm. oxygen pressure at 80° C.

Electrical Stability and Water Absorption of Deproteinized Rubber

From Boggs and Blake's publications (*8*, *9*) it might be implied that, when vulcanized rubber telegraph cables are immersed in water, they fail as a result of water absorption by the rubber. It is true that such cables show substantial increases in capacitance due to water absorption and that the signaling speed is more or less impaired by such increases. "Failure," however, implies a degradation to the point of uselessness. When complete failure does occur in vulcanized rubber cables in sea water, it is generally the result of local defects. Failures can result from the introduction into the insulation of water-soluble matter and heterogeneity by fillers or other compounding ingredients (*35*). Inclusion of foreign substances and mechanical defects also cause failure.

Rubber-insulated cables have been manufactured for many years and have given service for long periods. According to Hooper (*14*), 2700 miles of the Hooper vulcanized rubber submarine telegraph cable core were laid between 1868 and 1871, and more than 1300 miles were still in service in 1919; much of the core outlasted the armor.

On account of the osmotic nature of the water absorption process, immersion of cables in fresh water greatly increases the need for the use of purified rubber if the utmost electrical stability is desired. A comparison between the water absorp-

tion of deproteinized and plantation grades of rubber in distilled water is shown in Figure 2. In these tests the rubber was milled 10 minutes on a warm mill and pressed between Cellophane sheets in a mold at 105° C. to hold the thickness to close limits. The Cellophane was removed after the sheets had been cooled. In Table V the electrical properties and water absorption of a vulcanized pure gum rubber composition containing crepe and the same compound made from crepe purified by treatment with concentrated ammonia under pressure are compared. Sheets of these compositions 0.1 cm. in thickness were measured dry and after an extended period of immersion in distilled water. These data show a substantial reduction in water absorption and an increased stability of capacitance resulting from purification.

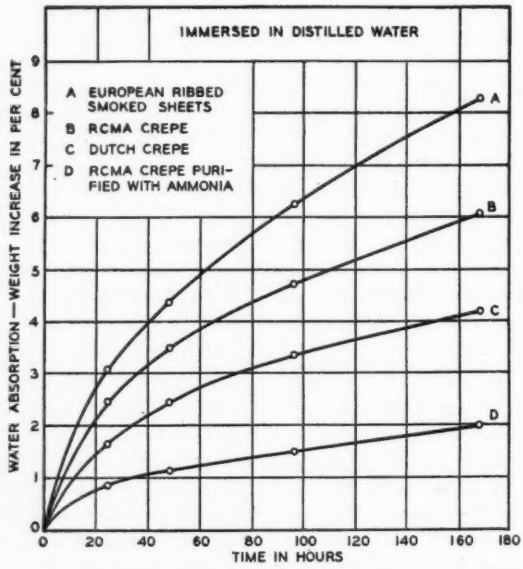

FIGURE 2. EFFECT OF PURIFICATION ON WATER ABSORPTION OF RAW RUBBER IN DISTILLED WATER AT 25° C.

(Sheets 0.0675 cm. thick)

It must be kept in mind that the method and extent of washing, as well as the freedom of wash water from salts, have an influence on the water absorption of the final product. If the proteins which enclose water-soluble matter are first rendered water soluble by chemical means, the removal of water-absorbing substances by washing is more readily accomplished and more complete. Although the ash and nitrogen contents of the final product are indicative of water-absorbing characteristics, they are not controlling, since ash may be affected by iron from the washing rolls. The nitrogen content is no in-

TABLE V. EFFECT OF PURIFICATION ON ELECTRICAL STABILITY AND WATER ABSORPTION OF VULCANIZED RUBBER[a]

	N_2 Content	Water Absorption[b]	Dielectric Constant[c] Dry	Dielectric Constant[c] Wet	Power Factor[c] Dry	Power Factor[c] Wet	D. C. Resistivity Dry	D. C. Resistivity Wet
	%	%			%	%	*Ohm-cm.*	*Ohm-cm.*
Plantation crepe, R. C. M. A.	0.35	6.01	2.50	3.03	0.23	0.34	$>5 \times 10^{15}$	0.7×10^{15}
Ammonia-purified[d] crepe	0.15	2.48	2.51	2.69	0.24	0.34	$>5 \times 10^{15}$	Not detd.
Ammonia-purified[e] crepe	0.05	1.58	2.51	2.56	0.23	0.30	$>5 \times 10^{15}$	2.1×10^{15}

	Parts by Weight
Rubber	100.00
Zinc oxide	1.00
Sulfur	0.75
Tetramethylthiuram monosulfide	1.00
Diphenylguanidine	0.20
Phenyl-α-naphthylamine	2.00

[a] Compn. (vulcanized 35 min. at 126° C.).
[b] After 135-day immersion in 3.5 per cent NaCl, followed by 41 days in distilled water at room temp.
[c] Measured at 2000 cycles per second and room temp.
[d] R. C. M. A. crepe heated 2 hr. at 109° C. in concd. NH_4OH, and washed 10 min. on creping rolls.
[e] R. C. M. A. crepe heated 2 hr. at 148° C. in concd. NH_4OH, washed 10 min. on creping rolls.

dication of the presence of nitrogen-free water-soluble matter. Water absorption tests must, therefore, be resorted to in order to judge the quality of purified rubber for electrical purposes. Measurement of the water absorption and changes in the dielectric properties of the rubber in a pure gum mix, as shown in Table V, provides a satisfactory method of evaluation since the object of purification is primarily the improvement in insulating characteristics.

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The Use of Acetylene in the Rubber Industry

Paul Walter

INTRODUCTION

The present paper on the use of acetylene and of calcium carbide in the rubber industry is subdivided into several different but interrelated sections.

Each section covers a definite phase of the subject, in fact this subdivision of the text was made with a view to the greatest clearness in dealing with the subject matter. From a technical point of view, each section deals in turn with general considerations, processes now in common use industrially, the application of acetylene to the manufacture of the particular products, the importance of the new process, and the results obtainable.

From an economic point of view, the sections deal with present production of the particular types of products, the likely proportions of calcium carbide and acetylene which would be used, and estimates of the possible consumption of these raw materials.

The subjects of the five sections are as follows:

I. Action of acetylene on rubber.

II. Fixation of acetylene by rubber.

III. Use of acetylene in the manufacture of tennis balls, balloons, and all dilated rubber articles in general.

IV. Use of acetylene in the manufacture of sponge rubber articles.

V. Action of acetylene on latex, and its use in the manufacture of sponge rubber particles and of crepe from latex.

I. THE ACTION OF ACETYLENE ON RUBBER

The effects of various gases on rubber have been a subject of study for many years, and numerous publications which will not be discussed here have appeared. It seemed of particular interest to the present author to study the action of acetylene on rubber by two distinct methods.

(1) the direct action of acetylene gas on rubber mixtures;

(2) the action of calcium carbide on the same rubber mixtures.

The Direct Action of Acetylene on Rubber.—It is known that rubber is a mixture of more or less definite complex hydrocarbons, and it may be assumed that acetylene, which is an unsaturated hydrocarbon, can be fixed by rubber. It would be misleading to give at this time formulas to represent the combination which takes place. It is questionable whether simple physical solution of the gas is involved or on the contrary whether there is chemical combination, with formation of addition products, polymerization products, etc. If addition compounds are formed, it is impossible in the present state of our knowledge to state precisely at what point in the cyclic chain the acetylene molecule combines. An investigation of this particular problem would seem to be of only theoretical interest, for in view of the fact that different rubbers vary in composition, not only when they are of different origin but even when they are from the same source, any conclusion would be confined to the specific case concerned, and therefore would be valueless. Further-

more this is not the desired objective, since in the final analysis the important question at issue is the action of acetylene on rubber.

To study this problem, various rubber mixtures, either in powder form or in thin sheets, were placed in a pressure bomb; acetylene was introduced by the method customarily used by the present author for other gases, *i. e.*, from a cylinder of compressed gas.

Two rubber mixtures were studied, one containing 90 per cent, the other 50 per cent of rubber; no antioxidant was added to either one. These mixtures were exposed to acetylene under pressures of 1 kilogram and of 5 kilograms for 12 hours, 48 hours, and 1 week, at temperatures of 18°, 50°, and 70° C.

The results of the tests are recorded in the table below. It can be concluded from these results that:

(1) Acetylenated rubber ages better in an oven test than does rubber not treated with acetylene.

(2) Acetylenated rubber ages better in a bomb under pressure, and the extent of this improvement is proportional to (*a*) the time of contact of the acetylene and rubber, and (*b*) to the pressure of the acetylene.

The samples in sheet form were placed in the bomb mentioned above, and after treatment discs were cut for permeability tests, samples for bomb aging tests, and other samples for tensile tests, according to ordinary technic.

The results of these tests are also recorded in the table, and they lead to the following general conclusions:

(1) When a rubber mixture is treated with acetylene, the permeability of the mixture is inversely proportional to the pressure of the acetylene in contact with it, to the time of contact, and to the surrounding temperature.

(2) The longer the time that the mixture is in contact with acetylene and the higher the pressure of the latter, the better is the aging of the mixture.

The results shown in the table indicate further that prolonged treatment, at high pressure, of a rubber mixture with acetylene retards its complete deterioration by the energetic treatment which it undergoes in the bomb test.

Action of Calcium Carbide on the Same Rubber Mixtures.—It is obvious that calcium carbide can be effective only if it is incorporated in a rubber mixture. Calcium carbide itself is inactive, and becomes effective only in virtue of the acetylene which it can liberate in contact with water. The acetylene thus set free forms cells in an unvulcanized rubber mixture.

The preparation of sponge rubber in this manner is discussed in Section IV, which deals with the use of acetylene in the manufacture of sponge articles. If crepe is desired, it is necessary only to pass the spongy unvulcanized rubber through a washing machine to destroy the cells, and the crepe containing acetylene is ready for use.

The developments so far described in a preliminary way lead to the general conclusion that acetylene has a beneficial effect on rubber in three ways:

(1) It diminishes or retards deterioration on aging.
(2) It diminishes its permeability.
(3) Its plasticizes rubber.

II. FIXATION OF ACETYLENE BY RUBBER

The interest from a technical point of view of fixing acetylene by rubber has already been pointed out. The process of bringing about this fixation on an industrial scale will next be discussed.

Table of Results

Gas and Its Pressure	Time of Exposure	Percentage of Rubber in Sample	Condition after Aging in Hot-Air Oven at Temperature Given			Permeability Carbon Dioxide + Oxygen under 5 Kg. Pressure at 70° C.		Aging in Bomb
			18° C.	50° C.	70° C.	Passage of Gas in Cc. per Week	Condition of Membrane after Test	Condition after Aging
Acetylene (1 kg.)	12 hours	50	Not sticky	Not sticky	Sticky	...	.....	.....
		90	" "	" "	"	710	Very sticky	Decomposed
	48 hours	50	Not sticky	Not sticky	Slightly sticky	...	.....	.....
		90	" "	" "	" "	680	Very sticky	Very sticky
	1 week	50	Not sticky	Not sticky	Slightly sticky	...	.....	.....
		90	" "	" "	" "	210	Slightly sticky	Sticky
Acetylene (5 kg.)	12 hours	50	Not sticky	Not sticky	Not sticky	...	.....	.....
		90	" "	" "	" "	350	Excellent	Very sticky
	48 hours	50	Not sticky	Not sticky	Not sticky	...	.....	.....
		90	" "	" "	" "	325	Excellent	Slightly sticky
	1 week	50	Not sticky	Not sticky	Not sticky	...	.....	.....
		90	" "	" "	" "	105	Excellent	Good
Nitrogen (control)	12 hours	50	Not sticky	Not sticky	Not sticky	...	.....	.....
		90	" "	" "	" "	750	Decomposed	Decomposed
	48 hours	50	Not sticky	Not sticky	Not sticky	...	.....	.....
		90	" "	" "	" "	730	Decomposed	Decomposed
	1 week	50	Not sticky	Not sticky	Not sticky	...	.....	.....
		90	" "	" "	" "	735	Decomposed	Decomposed

Technic of Acetylenation

There are several processes by which acetylene can be fixed by rubber:

(1) Fixation by raw rubber.
(2) Fixation by a rubber mixture before vulcanization.
(3) Fixation by the finished rubber article.

(1) *Fixation of Acetylene by Raw Rubber.*—This process can be carried out by evacuating an autoclave containing the rubber, heating at 70° C., filling with acetylene, letting the substances react for the required time, and lowering the temperature slowly. To assure a large surface area of contact, it is of advantage to have the rubber in finely divided form; and to promote the fixation of the acetylene on the rubber, the gas should be introduced under pressure into the autoclave.

When calcium carbide is employed, it is mixed into the rubber on a mill in the conventional manner, and the mixture is then placed in an autoclave with live steam. When the operation is finished, the product must be washed with a large amount of water in order to remove the lime which has been formed.

(2) *Fixation of Acetylene by a Rubber Mixture before Vulcanization.*—The procedure described above is followed in this case too. Although this method is the most general one for adding acetylene to rubber, it is applicable to rubber mixings only under certain conditions, because of the reactions which may take place between the lime and the various components, including fillers, in the rubber mixture; and also because many mixings, though not all, begin to vulcanize at 100° C., the temperature of the steam-autoclave.

(3) *Fixation of Acetylene by a Finished Product.*—This method has extremely limited application, and is useful only for thin articles, for after vulcanization acetylene gas can act only on the surface, *i. e.*, cannot penetrate into the rubber, and it does not combine so readily with vulcanized rubber as with raw rubber. For these reasons it would seem advisable to treat the rubber articles with acetylene in a rotary drum at a relatively low temperature and under pressure.

Economic Considerations

It would be interesting to make an estimate of the possible consumption of acetylene if applied to the treatment of rubber. Unfortunately, however, it seems impossible to obtain any idea of the extent of this consumption, first of all, because it would be wrong to assume that all rubber would be acetylenated by the methods described in spite of the advantages to be gained, and, secondly, because even if an estimate of the tonnage were to be made, the figure would be uncertain, because the quantity of acetylene fixed in a given case would depend primarily on the method utilized, and no account would be taken of the losses of gas which did not remain held by the rubber. For the present, nothing more definite can be said, but in any event it would seem that this fixation process would consume enormous quantities of acetylene.

III. THE USE OF ACETYLENE IN THE MANUFACTURE OF RUBBER BALLS, BALLOONS, AND DILATED ARTICLES

In principle, all dilated rubber articles are prepared in the same general manner. The articles, all of which are molded in a press, are prepared in two unvulcanized sheets between which is placed a pellet of a mixture of chemicals which evolve nitrogen when heated. In the press, the two sheets unite, and when heat is applied, nitrogen is liberated, with the result that the sheets expand and conform to the shape of the upper and lower halves of the mold. Vulcanization fixes in permanent

form the desired shape of the article, and the nitrogen remains under pressure (usually of the order of several hundred grams).

The Process Now in Use.—The method most frequently employed is the formation of nitrogen by the well-known reaction of sodium nitrite and ammonium chloride:

$$NaNO_2 + NH_4Cl \longrightarrow NaCl + 2H_2O + N_2.$$

Based on this reaction, it is evident that every 68 grams of sodium nitrite which react with 53 grams of ammonium chloride evolve 22.4 liters of nitrogen (at 0° C. and 760 mm. pressure). This process is simple and of practical utility, but involves two inconveniences: (1) Nitrogen is a gas which passes easily through rubber and (2) nitrogen is an inert gas at least under the conditions involved, and has no influence on the aging of rubber.

Introduction of Acetylene in the Manufacturing Process.—There are several ways of carrying this out successfully. A method may be described which is analogous to the nitrite process, and also utilizes a chemical reaction. In place of using a pellet of sodium nitrite-ammonium chloride mixture, a pellet of calcium carbide is used under exactly the same conditions. Water is necessary for the liberation of acetylene, and this can be obtained in various ways, notably by the use of salts containing a large number of molecules of water of crystallization. Of these salts, the principal ones are:

Salt	
$Al_2(SO_4)_3.18H_2O_2$	342 grams give 324 grams of water
$Al_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$	475 grams give 438 grams of water
$MgCl_2.6H_2O$	95 grams give 108 grams of water
$Na_2HPO_4.12H_2O$	142 grams give 816 grams of water
$Na_2CO_3.10H_2O$	106 grams give 180 grams of water
$Na_3PO_4.12H_2O$	164 grams give 216 grams of water

All these salts fuse in their water of crystallization when heated at vulcanizing temperatures. The selection of a suitable salt depends on: (1) its market price; (2) the rate at which it liberates its water of crystallization; (3) the composition of the rubber mixture, and (4) the mode of storage of the compressed salt-calcium carbide mixtures.

The following dry mixture containing sodium carbonate is representative of what may be successfully used:

Calcium carbide (coarsely powdered)	100
Sodium carbonate (coarsely powdered)	100
Saponifiable oil (*e. g.*, rosin oil)	20

After first intimately mixing the calcium carbide with one half of the oil and separately the sodium carbonate with the other half of the oil, the two halves are thoroughly mixed and compressed into suitable units.

At the temperatures employed for vulcanization, the water of the sodium carbonate is liberated, the calcium carbide is decomposed thus: $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$, and the sodium carbonate and the calcium hydroxide saponify the oil.

In cases where the particular salts which are chosen are too sensitive or rapid in their action, the compressed mixtures should be prepared at the moment when they are to be used.

It is also possible to utilize water with or without a saponifying agent, in which case the water is added when the sheets are prepared on a mill, merely by pouring

it directly on the calcium carbide-oil mixture. There are still other ways of carrying out the process.

The quantity of calcium carbide to be used can be estimated simply by measuring the volume of the article to be dilated; then knowing the pressure desired, a simple calculation gives the necessary weight (1 kilogram of calcium carbide liberates approximately 380 liters of acetylene).

This process of manufacturing balls, balloons, and dilated articles is of particular interest for two reasons: (1) because of the favorable influence of acetylene on rubber, and (2) because of the slow diffusion of this gas through the walls of an article.

The cost of the process depends to a large extent on the particular modification which is adopted. In all cases it is of the same general order as the cost of the sodium nitrite-ammonium chloride process, if not in fact a little more economical. A conservative estimate would point to a daily production of 1,000,000 dilated rubber articles in all countries. If it is assumed that each object would require 4 grams of calcium carbide, the total consumption of carbide would be 4 tons per day, or 800 tons each year of 200 working days.

IV. THE USE OF ACETYLENE IN THE MANUFACTURE OF SPONGE ARTICLES

In this discussion sponge articles are considered to be all articles with a cellular structure; the prototype is the toilet sponge, but to the list could be added mats, cushions of all kinds, etc.

Present Process.—In the process now generally used, sodium bicarbonate or ammonium carbonate is added to the rubber mixture; at the temperature of vulcanization the sodium bicarbonate decomposes and liberates carbon dioxide; ammonium carbonate also liberates ammonia.

When either of these salts is intimately mixed with rubber, it is evident that each discrete evolution of gas forms a cell; hence the cellular character of sponge rubber produced by this process.

Use of Calcium Carbide in the Manufacture of Sponge.—Sodium bicarbonate or ammonium carbonate is merely replaced by calcium carbide, the fineness of which depends on the size of cell desired in the sponge rubber. Though not absolutely necessary, it is recommended that, for ease of processing, the calcium carbide be intimately mixed with a saponifiable oil, and that a crystalline salt be used, as described in Section III. The technic is then the same as before.

Under these conditions the calcium hydroxide which is formed functions as an accelerator of vulcanization, and allowance must be made for this in formulating the rubber mixture. If an acidic accelerator is employed, it may possibly combine with the calcium hydroxide.

A typical recipe for manufacturing sponge rubber by the acetylene process is the following:

Rubber	100
Sulfur	3.2
Accelerator	0.5
Zinc oxide	5
Calcium carbide	10
Sodium carbonate	10
Saponifiable oil	15

The acetylene process is of particular interest because of the low price of calcium carbide compared with that of sodium bicarbonate and that of ammonium carbonate, because of the possibility of controlling the size of the pores or cells by the proper choice of size of particle of the carbide, and finally because of the generally beneficial effect of acetylene on rubber, as described in Section I.

Economic Considerations.—The world production of sponge rubber products may be estimated to be very roughly 14 tons per day. If it is assumed that this amount requires 7 per cent of calcium carbide, *i. e.*, the same percentage as of sodium bicarbonate or ammonium carbonate, the consumption would be 980 kilograms, in other words, around 1 ton, of calcium carbide per day, or around 200 tons for a year of 200 working days.

V. THE ACTION OF ACETYLENE ON LATEX. ITS USE IN THE MANUFACTURE OF SPONGE RUBBER ARTICLES MADE FROM LATEX

(In Collaboration with M. Leduc)

Calcium carbide, coated with a saponifiable oil, is added to the uncoagulated liquid latex. The ammonia in the latex commences at once to saponify the oil which envelops each particle of carbide, and as soon as acetylene is liberated the resulting calcium hydroxide also saponifies the oil, with formation of calcium soaps. Both the calcium hydroxide and the calcium soaps coagulate the latex completely. The evolution of acetylene is sufficient for the formation of sponge products which can be utilized in various ways.

Manufacture of Ordinary Articles.—Sponge prepared from latex in the manner described can, while still unvulcanized, be passed through a washing mill, where the pores are destroyed; the product, which is ordinary crepe, except that it is impregnated with acetylene, is ready for conventional use.

Manufacture of Sponge Articles.—By operating in the same way, but adding the proper compounding ingredients to the latex, the spongy products which result can be vulcanized immediately without any special precautions.

The following is a typical recipe for a product manufactured in this way:

Latex (60 per cent)	160
Rapid accelerator (a diethyldithiocarbamate)	0.4
Zinc oxide (aqueous dispersion)	2
Ammonium sulfate	0.4
Aqueous casein	10
Calcium carbide-saponifiable oil	4

It should be noted that the dilution of the latex governs the thickness of the cell walls, the size of the particles of calcium carbide governs the dimensions of the cells. The proportion of oil to calcium carbide controls the rate of coagulation of a particular latex. The proportion of calcium carbide to rubber controls the formation of the cells for a particular latex.

There is a modification of this process for the manufacture of sponges which simplifies the operations, *viz.*, to add the calcium carbide directly to the latex. By cautious agitation, acetylene is liberated, forms cells, and the calcium hydroxide formed coagulates the latex.

This process of manufacturing sponge rubber is of interest because of the economy in the sponging agent, and also as before there is the advantage of the beneficial effect of the acetylene on the rubber.

Economic Considerations.—In this process in particular, it is still more difficult to estimate the possible consumption of calcium carbide. It can only be said that the world consumption of latex is at present around 25,000 tons. If two per cent of calcium carbide (based on the latex) were to be used, and this is only a hypothetical figure, there would be an annual consumption of 500 tons of calcium carbide.

CONCLUSIONS

Considering the advantages to be gained as a result of the favorable effect which acetylene has on rubber, it would be of still greater interest to study: (1) the

coagulation of latex by acetylene, and (2) the fixation of acetylene by reclaimed rubber and by factice. Such studies should be of great significance, and if successful results were to be obtained, a large market for calcium carbide would be created.

The use of calcium carbide in the rubber industry is of interest at present in three ways:

(1) Its technical advantages, including the improvement to be gained in the quality of the rubber products, and the simplification of manufacturing operations.

(2) Its economic advantages, *i. e.*, the lower costs.

(3) Its consumption, which, though impossible to foresee even in an approximate way, is possibly indicated by the following estimates:

Balls and balloons	800 tons per year
Sponge articles	200 tons per year
Latex products	500 tons per year
	1500 tons per year

This total of 1500 tons per year is not of great significance, because it would be misleading to assume that all the manufacturing plants which make the articles described would use calcium carbide. To offset this, it has just been mentioned that there would be a very large consumption of calcium carbide if latex were to be coagulated by acetylene, or indirectly by calcium carbide, by some economical process, as seems possible.

In conclusion, there are always unexpected uses for calcium carbide and acetylene in the rubber industry.

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Tests on Crepe Soling

III. Water Absorption

T. H. Messenger and J. R. Scott

INTRODUCTORY

In experiments on the softening of soling crepe by immersion in hot water (*J. Res. Assoc. Brit. Rubber Manufrs.*, **5**, 64 (1936)) it was noticed that in some cases considerable amounts of water were absorbed. This suggested that water absorption might prove to be useful in distinguishing between factory and estate crepes, and might bear some relationship to other important properties of the material, *e. g.*, tensile strength and solution viscosity. Water absorption is important also in connection with the use of crepe soling for footwear, but no information on water absorption with special reference to this use was found in the literature. It may be noted, however, that water absorption by raw rubber is considered to be due mainly to water-soluble components and proteins, which are unable to diffuse out through the rubber, or do so only very slowly, and therefore take up water to form an internal solution, the rubber acting as a semi-permeable membrane allowing only water to pass. The concentration of the internal solution decreases by imbibition of water until the difference between its osmotic pressure and that of the external liquid just balances the elastic pressure exerted by the distended rubber (cf. Lowry and Kohman, *J. Phys. Chem.*, **31**, 23 (1927); Bell Telephone Laboratories Reprint **B-228**; Boggs and Blake, *Ind. Eng. Chem.*, **18**, 224 (1926); Brown, *Bull. Rubber Growers' Assoc.*, **7**, 524 (1925); Williams and Kemp, *J. Franklin Inst.*, **203**, 35 (1927); Bell Telephone Laboratories Reprint **B-227**).

EXPERIMENTAL

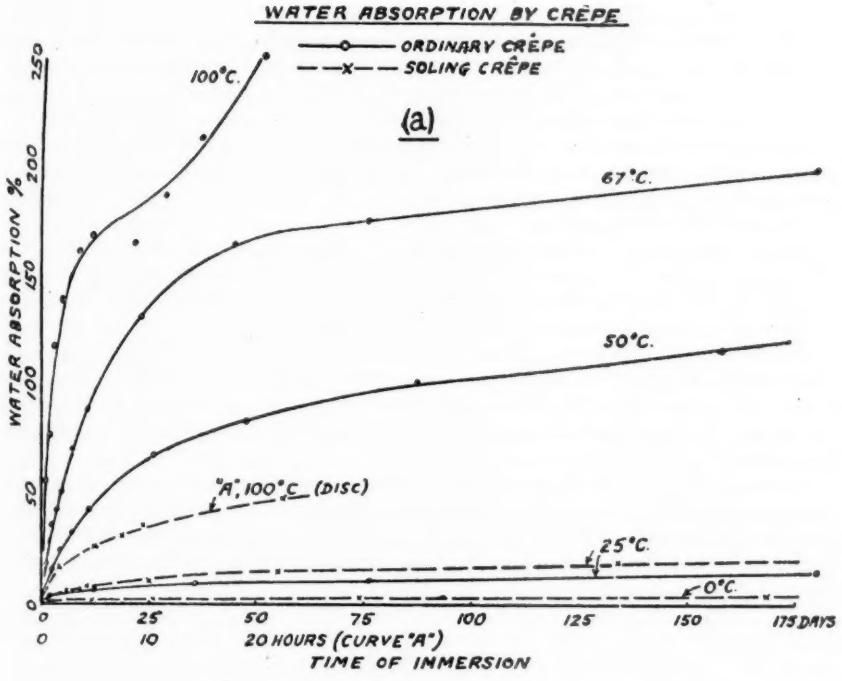
Method of Measuring Water Absorption

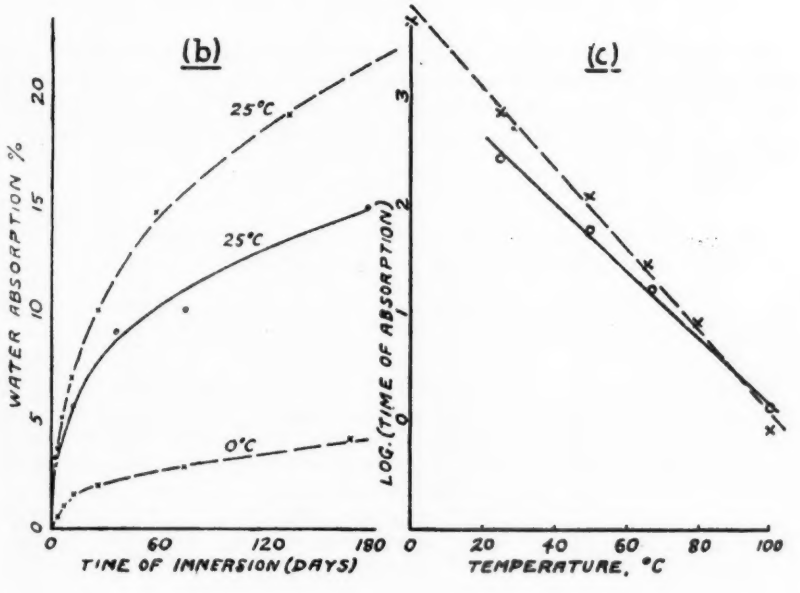
The rubber was thoroughly wetted by immersion in water at 25° C., then dried with a cloth, and kept in a vacuum desiccator for 30 minutes, this period having been found by experiment to be the most suitable. After being weighed, the rubber was immersed in water under the required conditions, then removed, dried as described, and weighed. The increase in weight, expressed as a percentage of the weight of the original rubber, was taken as the water absorption. During the immersion, care was taken to keep the rubber completely under the water.

Absorption from Pure Water

The Absorption Curve.—Fig. (*a*) shows the absorption from distilled water at various temperatures by (1) ordinary pale crepe, cut into thin strips; (2) soling crepe No. 42 (see Table II) in the form of rings, cross section 2.2 × 6 mm.; and (3) a disc of the same soling crepe, 45 mm. diameter and 6 mm. thick (curve "A," plotted on a more open time scale). The curves for 0° and 25° C. are replotted on more convenient scales in Fig. (*b*).

None of these curves reaches an equilibrium value, but in many cases there is a considerable falling off in the rate of absorption after a time, so that the curves approach the form characteristic of the swelling of vulcanized rubber. The ab-


WATER ABSORPTION BY CREPE
ORDINARY CREPE
SOLING CREPE
(a)
100°C.
67°C.
50°C.
"A", 100°C (DISC)
25°C.
0°C.
WATER ABSORPTION %
0
50
100
150
200
250
0
25
50
75
100
125
150
175 DAYS
0
10
20 HOURS (CURVE "A")
TIME OF IMMERSION


(b)
25°C
25°C
0°C
WATER ABSORPTION %
0
5
10
15
20
0
60
120
180
TIME OF IMMERSION (DAYS)
(c)
LOG. (TIME OF ABSORPTION)
0
1
2
3
0
20
40
60
80
100
TEMPERATURE, °C

sence of an equilibrium value for raw rubber swelling in water under ordinary conditions has been observed by Boggs and Blake (*loc. cit.*), Williams and Kemp (*loc. cit.*), and Obach ("Die Gutta-percha," Berlin, **1899,** 66, 105; Kirchhof, *Kolloid Z.*, **35,** 367 (1924)). Williams and Kemp, however, found that in oxygen-free water, equilibrium was attained; the slow continued increase in absorption in presence of oxygen must therefore be due to a gradual change in the rubber induced by oxidation, exactly as in the swelling of vulcanized rubber. It appears, therefore, that the water absorption curve for raw rubber is analogous to the swelling curve for vulcanized rubber in organic liquids, involving an initial comparatively rapid saturation, and a slow, indefinitely prolonged increase or "increment" caused by a change in the properties of the rubber.

When crepe which has absorbed water is kept in a vacuum desiccator, water is lost rapidly at first, but later at a gradually decreasing rate, the drying curve being roughly similar to the absorption curve, though of course inverted; the form of the drying curve differs somewhat from rubber to rubber.

Influence of Temperature.—Figs. (*a*) and (*b*) show that water is absorbed much more readily at higher temperatures. This was confirmed by additional experiments with soling crepe No. 42; rings of cross section 2.2 × 6 mm. were immersed in distilled water, with the results shown in Table I (the 0° and 25° C. results are those already given in Figs. (*a*) and (*b*).

If the logarithm of the time required to absorb a given small amount of water is plotted against temperature, the points lie approximately on a straight line, and the same result is found in the experiments on ordinary crepe already described (see Fig. (*c*)). The influence of temperature on rate of absorption can therefore be represented by the equation:

$$R = R_0 K^{t/10}$$

where R = rate of absorption at t° C.
R_0 = rate of absorption at 0° C.
K = temperature coefficient for an interval of 10° C.

The value of K is 2.5 for the soling crepe (Table I) and 2.1 for ordinary crepe, in good agreement with the results of other workers, *e. g.*, 2.6 (Kirchhof, *Kolloid Z.* **35,** 367 (1924) and 2.2 (calculated from data of Lowry and Kohman, *loc. cit.*)); a lower value, 1.6, is obtained by applying the above method to Boggs and Blake's data (*loc. cit.*).

TABLE I

Temperature	Time, Days	Absorption, %	Temperature	Time, Mins.	Absorption, %
0° C.	1	0.49	50° C.	250	1.92
	3	0.57		550	3.10
	7	1.03		1400	6.94
	12	1.56			
	26	1.91	67° C.	50	1.54
	74	2.80		120	3.48
	168	4.07		250	5.54
25° C.	2	2.85	80° C.	32	3.12
	3	3.60		62	5.11
	6	5.10		100	7.29
	11	6.94			
	25	10.0	100° C.	8	5.52
	58	14.5		18	9.1
	134	19.1		30	9.6

The rapid increase in rate of absorption with rise of temperature cannot be ascribed entirely to the reduction in the viscosity of water nor to the increase in the osmotic pressure of the internal solution, as the temperature coefficients of these properties are 1.2 and 1.03, respectively, for a temperature difference of 10° C. The permeability of rubber to fluids, however, has a temperature coefficient of about 1.6 (Daynes, *Trans. Inst. Rubber Ind.*, **3**, 428 (1928)), and according to the data of van Rossem and van der Meyden (*India-Rubber J.*, **76**, 360 (1928)) the rate of plastic deformation of raw rubber under load, which must influence water absorption since this involves progressive deformation of the rubber, has a temperature coefficient of about 3.0; these factors probably contribute largely to the high temperature coefficient for rate of water absorption. Comparison of the results in Table I with those in Part II of this series shows that the softening of the rubber by heat (where this occurs) is complete before an appreciable amount of water is absorbed, so that the rate of softening, which varies greatly with temperature, has little influence on water absorption.

The temperature coefficients given above do not hold for the later parts of the absorption curves, as the absorption at low temperatures falls considerably below the value calculated from the higher temperature curves. This is probably an indication that the water absorption at low temperatures is tending to approach an equilibrium value, in accordance with the suggestion already made that the absorption curves are roughly of the type observed with vulcanized rubber, in which an approximate equilibrium is attained. It appears, therefore, that rise of temperature increases not only the initial rate of absorption, but also the water-absorbing capacity of the rubber. This may be ascribed mainly to the great decrease in the rigidity of the rubber which enables the osmotic pressure of the water-soluble components to produce a greater distension of the rubber; this influence of varying rigidity on water absorption has been observed experimentally in thermoplastic materials by Lowry and Kohman (*loc. cit.*).

Tests on a Range of Soling Crepes.—A number of soling crepes, including estate- and factory-prepared types, were examined by punching out discs 45 mm. diameter and immersing these for 5 hours in distilled water at 100° C. (see Table II); the accuracy of these results was checked by repeat experiments on some of the samples, the duplicate results being in good agreement. Samples Nos. 1 to 27 have already been described (*J. Res. Assoc. Brit. Rubber Manufrs.*, **3**, 127 (1934)), where the results of mechanical and chemical tests and viscosity measurements are given. Ply-adhesion was tested by hand after softening the crepe in boiling water; the terms "good" and "bad" used in this connection are purely relative, as only in two cases was the ply-adhesion really unsatisfactory.

The most striking feature of these results is the enormous variation in water absorption between different samples. Several causes may contribute to this variation:

(*a*) Differences in amount and nature of the water-soluble components; this alone cannot be considered adequate to explain a variation between 0.8 and 29% absorption.

(*b*) Differences in mechanical properties, since the rate of absorption should depend on the resistance of the rubber to deformation; from the results given already (*J. Res. Assoc. Brit. Rubber Manufrs.*, **3**, 127 (1934)), for samples Nos. 1 to 27, however, there is no evidence of a close relationship between water absorption and either rigidity or rate of plastic deformation under a small load.

(*c*) Penetration of water between the plies, the number of which varies considerably. As only the initial stage of absorption is under consideration, the amount absorbed depends mainly on the area of exposed rubber surface. If wates does not

TABLE II

Estate Crepes				Factory Crepes			
No.	Thickness, Inch	No. of Plies, and Ply-Adhesion[a]	Water Absorption, %	No.	Thickness, Inch	No. of Plies, and Ply-Adhesion[a]	Water Absorption, %
4	0.25	2 M	2.7	1	0.16	2 M	10
5	0.13	2 G	2.5	2	0.09	1	9.0
6	0.13	2 G	4.7	3	0.13	1	7.0
7	0.22	2 B	13	20	0.16	2 G	3.2
8	0.06	1	19	21	0.31	3 M	1.6
9	0.25	5 M	15	22	0.16	3 G	3.4
10	0.25	5 G	3.5	23	0.31	6 B	9.1
11	0.16	4 M	23	24	0.31	4 B	9.7
12	0.16	4 G	2.6	25	0.16	1	3.6
13	0.16	4 M	16.4	26	0.31	10 B	17
14	0.09	3 G	11	27	0.44	13 B	21
15	0.13	3 M	6.2	28	0.16	2 M	5.7
16	0.13	3 G	3.7	30	0.28	4 G	0.9
17	0.13	3 G	3.5	31	0.31	4 G	1.0
18	0.13	4 M	12	43	0.31	3 M	7.9
19	0.13	3 B	15	44	0.28	3 G	2.1
29	0.13	3 M	12	45	0.31	3 G	3.0
32	0.16	2 B	11	46	0.28	4 G	1.1
33	0.28	6 B	14	47	0.28	4 G	1.1
34	0.13	4 G	13	48	0.28	4 G	0.8
35	0.09	2 M	13	49	0.28	4 G	1.5
36	0.16	3 G	2.7	50	0.28	4 G	1.0
38	0.13	3 B	19				
39	0.13	3 M	13				
40	0.13	3 M	11				
41	0.28	9 G	1.1				
42	0.25	8 B	29				

[a] G, M, and B denote respectively good, medium, and bad ply adhesion.

penetrate between the plies, the exposed surface must be practically the same in all cases, and there should be a rough inverse relationship between percentage absorption and thickness; if there is perfect circulation of water between the plies, there should be an inverse relationship between absorption and the thickness of one ply. Actually, there are indications of inverse relationships in both cases, as is shown by dividing the crepes into groups according to total thickness and ply thickness, respectively, and averaging the results in each group (see Table III).

TABLE III

Total Thickness, Inch	Water Absorption, %	Ply Thickness, Inch	Water Absorption, %
0.08	13	0.03	15.3
0.13	9.5	0.04	11.5
0.16	8.2	0.05	8.8
0.26	6.2	0.06	8.7
0.33	8.8	0.07	1.1
		0.08	6.8
		0.10	6.1
		0.14	4.5

It appears, therefore, that water does penetrate between the plies, but not to such an extent that their entire surface is in contact with water. The same conclusion is indicated by calculating the absorption per unit area of ply surface, *i. e.*, total surface of all plies, when it is found that the absorption is, on the average, smaller the better the ply-adhesion, as would be expected if there was partial circulation between the plies (see Table IV).

Differences in ply-adhesion alone are not sufficient to explain the variation in water absorption; for instance, the difference between crepes Nos. 41 and 42, which have practically the same ply construction, is far greater than could be accounted for by assuming perfect ply-adhesion in one case and perfect circulation between the 8 plies in the other.

TABLE IV

Ply-Adhesion	Absorption per Unit Area of Ply Surface, G. per Sq. Cm.
Good	0.0018
Medium	0.0060
Bad	0.0085

(*d*) Differences in the permeability of the rubber to water; it is probable that rubber prepared by lightly rolling the coagulum has a spongy structure permeable to water, whereas further mechanical working, heating, or pressing compacts the structure and renders it less permeable. Differences in rate of absorption may therefore arise from differences in treatment during manufacture.

It might be anticipated that porosity would be indicated by low apparent specific gravity; in fact it is found that samples Nos. 11, 24, 26, and 27, which have abnormally low specific gravities, all have relatively high water absorption, but apart from this there is no obvious relationship between these properties.

Comparison of Estate and Factory Crepes.—Broadly speaking, the factory crepes absorb water less rapidly than the estate crepes (see Table V). This is partly accounted for by the greater average total thickness and ply thickness of the factory samples, which gives them a smaller average surface/volume ratio. The absorption per unit area of surface, however, is also smaller for the factory crepes; although this small difference may be accidental, it is in the direction which would be expected from the consolidating effect of heat and pressure mentioned in paragraph (*d*) above.

TABLE V

	Estate	Factory
Average thickness	0.16 in.	0.26 in.
Average ply thickness	0.049 in.	0.080 in.
Average water absorption	10.8%	5.5%
No. of samples with less than 2% absorption	1	8
No. of samples with 2 to 5% absorption	8	5
No. of samples with 5 to 12% absorption	6	7
No. of samples with more than 12% absorption	12	2
Absorption per unit area of outer surface[a]	0.020	0.016
Absorption per unit area of ply surface	0.0061	0.0050

[a] *i. e.*, top and bottom surfaces of sheet.

Correlation between Water Absorption and Other Properties.—With the present samples there appears to be no general relationship between water absorption and either solution viscosity, tensile strength, rigidity, or plastic yield as determined by the rate of elongation under a small load at 70° C.

Absorption from Aqueous Solutions

According to the theory of water absorption described in the Introduction, absorption should be reduced by increasing the osmotic pressure of the external liquid, *e. g.*, by using an aqueous solution instead of pure water. Obach, Boggs and Blake, Williams and Kemp, and Lowry and Kohman found that water absorption was

lowered by adding a soluble salt to the water, but their results do not lend themselves to testing the accuracy of the osmotic theory of water absorption, because the absorptions were mostly very small and in some cases only the initial part of the absorption curve was examined.

Experiments were therefore made with ordinary crepe kept at 35° C. in pure water and in solutions of various osmotic pressures, cane sugar being used for all but the lowest two pressures, which were obtained with Congo Red (see Table VI). These solutions were chosen because their osmotic pressures had already been accurately determined (Landolt-Börnstein Physikalisch-Chemische Tabellen, Berlin, 1912).

TABLE VI

WATER ABSORPTION (%)

Period of Immersion, Days	Osmotic Pressure (Atmospheres): 0	0.015	0.061	0.73	1.41	2.87	7.00	22.0	45.2
2	3.3	3.5	3.6	3.5	3.4	2.9	2.9	2.4	1.5
5	5.2	5.7	5.4	5.5	5.0	4.1	4.1	3.2	1.8
17	10.7	11.9	11.2	10.7	9.5	7.6	6.8	4.3	2.2
49	19.4	19.7	18.7	17.1	15.0	10.9	8.5	4.5	2.1
88	31.2	28.1	24.1	22.1	18.8	12.8	9.0	4.2	1.8
121	38.2	35.3	28.5	26.1	20.2	14.3	9.3	4.2	...
172	49.0	45.0	34.5	30.8	21.5	15.5	8.9	...	...

With the higher osmotic pressures, the water absorption reaches an approximate equilibrium value, which is lower the higher the osmotic pressure, as required by theory. Whether an equilibrium would be reached in the other cases cannot be said from these results.

The equilibrium absorption, after subtracting absorption by the rubber hydrocarbon itself (about 0.5% according to Lowry and Kohman, *loc. cit.*), should be related to the osmotic pressure of the external solution approximately according to the equation:

$$\frac{S \times 25000}{MA} - P = \frac{ADE}{100}$$

where A = water absorption (%) due to water-soluble matter;
S = percentage of water-soluble matter in rubber;
M = effective mean molecular weight of water-soluble matter;
P = osmotic pressure of external solution (atmospheres);
D = specific gravity of rubber;
E = modulus of volume elasticity of rubber (pressure required to produce 100% expansion).

This is found to be the case, and taking S as 0.4, E is of the order 10^7 dynes per sq. cm. (10 atmospheres) and M is about 140. The total absorption calculated from these values of E and M is compared with the observed value in Table VII.

TABLE VII

Equilibrium, Calculated	Absorption (%), Observed
22.9	23[a]
17.0	17[a]
9.7	9.1
3.7	4.2
2.1	2.0

[a] By extrapolation.

The agreement between calculated and observed values, and the fact that the value found for M is of about the magnitude which would be expected from the nature of the water-soluble components, confirm the view that water absorption by raw rubber is determined by the equilibrium between internal and external osmotic pressures and the volume elasticity of the rubber. The fact that the initial rate of absorption is not appreciably influenced except by high osmotic pressures (see Table VI) is also in accordance with theory, since the concentration, and therefore osmotic pressure, of the internal solution is initially very high, so that the force driving the water into the rubber is practically independent of the osmotic pressure of the external solution, provided this is small.

Summary and Conclusions

The main results obtained are summarized below:

(1) The following observations made by previous workers are confirmed. The absorption by crepe immersed in pure water continues for a very long time, if not indefinitely; the initial rate of absorption and the amount absorbed after long immersion increase rapidly with rise of temperature. The influence of temperature is probably due largely to its effect on the mechanical properties of the rubber, the softening induced by heat facilitating the distension of the rubber.

(2) Soling crepes vary enormously in rate of water absorption; this result is ascribable to a variety of causes, as there is direct evidence that water absorption is influenced by the number of plies and the ease of penetration of water between the plies, while the porosity (permeability) of the rubber and its content of water-soluble matter must also come into play; the rigidity of the rubber would be expected to have some influence, although this is not evident in the present experiments.

(3) Water absorption does not differentiate sharply between estate and factory-prepared soling crepes, though there are indications that on the average factory crepes absorb water somewhat less rapidly.

(4) Among the soling crepes examined, water absorption bears no obvious relationship to mechanical properties or solution viscosity.

(5) Addition of solutes to the water in which rubber is immersed reduces the water absorption, and this occurs quantitatively in accordance with the osmotic theory of water absorption.

These results indicate that water-absorption tests do not in general yield any information as to the mechanical or physical properties of crepe soling or its mode of manufacture, and are therefore of value only in relation to the water-absorbing properties of the material. Absorption at atmospheric temperatures is so slow that under normal conditions of use it probably does not affect more than a thin surface layer. This layer, however, is responsible for the grip of the soling on the pavement, and if absorption of water influences this gripping power, the control of water-absorbing capacity becomes important. The wide variation at present found between different crepes suggests that an investigation of the factors governing water absorption would enable this property to be closely controlled over a wide range.

Penetration of water between the plies, which will occur especially when the soling is somewhat worn, may be more serious than absorption at the outer surface, since water cannot readily dry out from between the plies, and the absorption may therefore become cumulative and lead to weakening of the ply-adhesion.

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Mastication and Rate of Set-Up

Part I

S. Buchan

Until comparatively recently the importance of rate of set-up measurements in rubber compounding and in factory control testing received very little attention, but within the last few years various methods have been devised and used by different investigators.

In many laboratories, the standard method of testing utilizes the change in physical properties which occurs when the rubber is converted from a plastic mass to an elastic solid under the influence of heat, the course of the reaction being traced by means of a plastometer. With a plastometer of the parallel plate type, such as the Williams instrument, a number of cylindrical test samples of known volume are cut from the mixed rubber under examination, and placed in the oven of the plastometer, maintained at a constant temperature. At definite intervals individual samples are tested on the plastometer and a note is made of their plasticities or, it may be, of their recoveries. When either of these sets of readings is plotted against the time of heating, it is usually observed in an accelerated mixing that the point at which vulcanization commences is shown by a steep inclination of the curve away from the time axis.

This method may be regarded as satisfactory at comparatively low temperatures, provided the times of heating between readings are fairly long. If, however, it is necessary to use a temperature as high as, say, 120° C. in order to reproduce processing or initial curing conditions, several factors must be taken into consideration, each of which tends to lessen the accuracy of the test. For example, opening and shutting the oven door at short intervals causes fluctuations in temperature, which are all the greater the higher the temperature. Also, as the heating elements in electrically controlled plastometer ovens are present usually in the walls and floor, the actual temperature on the floor is sometimes considerably higher than that recorded on a thermometer suspended above. It may be observed that the base of a sample resting on the floor of the oven, or on a piece of felt laid on the floor, tends to vulcanize more quickly than the upper portion. An example will be quoted later in the paper to show just how much these factors may influence comparative tests when the variations in rate of set-up are small.

When the extrusion, or Marzetti, type of plastometer is employed, the rubber is extruded under conditions of constant temperature and pressure, and the extruded cord is weighed and converted to a volume basis for comparative purposes. As the rubber tends to set-up the speed of extrusion falls, and this diminution is reflected in the weight of rubber extruded. As a means of evaluating a quality which is ultimately to be processed by extrusion, this method appears to be quite satisfactory. Because of its slowness of action, however, the extrusion plastometer is not so satisfactory as the parallel plate type in plasticity control testing, and consequently few laboratories in this country have this piece of apparatus at their disposal.

A further method of determining rate of set-up depends on the fact that unvulcanized and vulcanized rubbers differ markedly in their behavior towards organic solvents. Whereas unvulcanized rubber is readily soluble in many organic solvents,

vulcanized rubber is very sparingly so. If, therefore, samples of an unvulcanized mixed rubber are heated at constant temperature and, at intervals, individual samples are removed and immersed in a rubber solvent, such as benzene, then the course of reaction may be followed by measuring the diminishing solubilities of successive samples. Thies (*Ind. Eng. Chem.*, **20,** 1223 (1928); **23,** 1357 (1931)) developed this method still further, and estimated the degree of solubility by the state of dispersion in the solvent of one of the ingredients of the mixing.

Cany (*Rev. gén. caoutchouc*, **75,** 21 (1931)) suggested that if a solution of mixed rubber were placed in a thermostat and stirred, the degree of set-up of the rubber solution could be determined at any given time by observing the amount of power consumed in driving the stirrer. This method, however, does not appear to have found much favor, probably due to the fact that, in the gelling of solutions, factors other than the composition and nature of the rubber phase appear to play a large part.

In the course of their experiments on accelerators and retarders, Twiss and Jones described another method (*J. Soc. Chem. Ind.*, **54,** 13 (1935)). A small pellet of

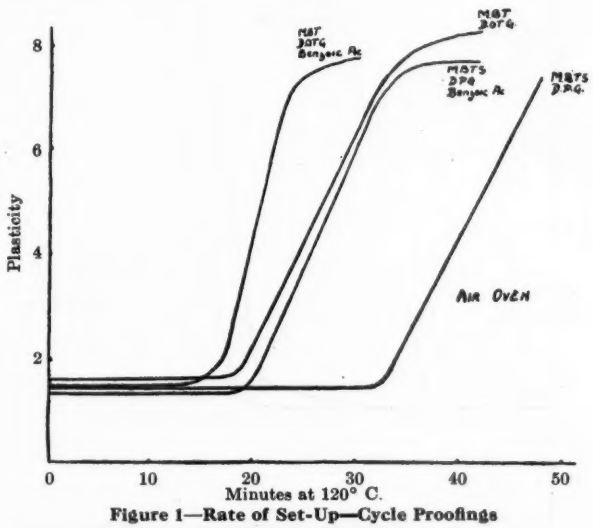

Figure 1—Rate of Set-Up—Cycle Proofings

rubber was immersed in a test tube containing glycerol, which in turn was placed in a glycerol bath kept at a constant temperature, and the course of the reaction was followed by prodding the rubber at intervals with a glass rod. By this means, apparently good and reproducible results were obtained with the accelerators under consideration, but it would appear that the human element is too pronounced for the test to become adopted generally as a means of measuring set-up. Moreover, the method indicates a point at which definite set-up has occurred, whereas it is the opinion of the writer that the stage at which set-up has occurred, is relatively unimportant compared with the initial stages of setting-up especially when progression from the beginning of the reaction to final set-up may occur very gradually and may take quite a long time, as is the case when weak acceleration is employed.

Several other methods of determining rate of set-up have been described in the literature such as undercuring stocks over a range of temperatures, whereby the

stock giving the best physical properties was adjudged the most likely to scorch; or milling or extruding mixed rubbers with various accelerators at high temperatures, and comparing the times taken before the respective qualities ceased to mill or extrude smoothly.

The methods outlined above are, however, open to criticism on one or more of the following grounds: (1) they cannot be used to reflect processing conditions, especially conditions of temperature, (2) they do not indicate the changes that occur during the initial stages of the reaction, (3) they are not sufficiently accurate to show small differences in the rate of set-up, and (4) they are too unwieldy to be employed as a factory control test.

In all experiments with mixed rubber described later in this paper, rate of set-up measurements were carried out as follows. A number of samples, 2 cc. in volume,

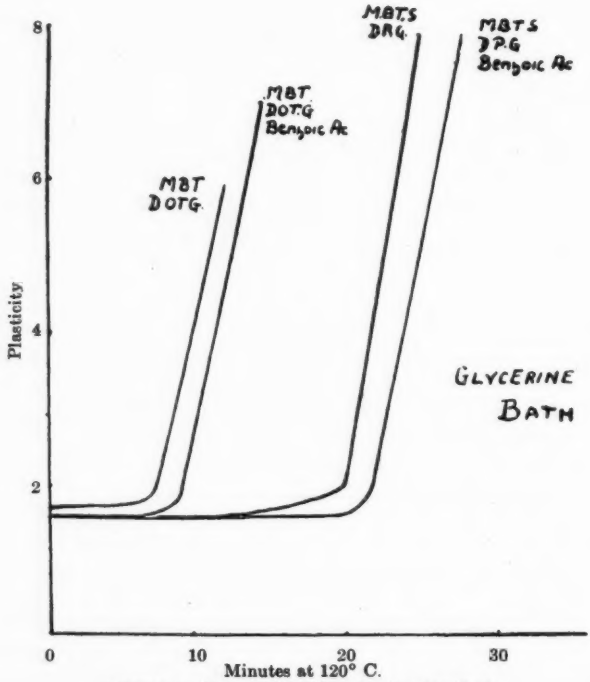

Figure 2—Rate of Set-Up—Cycle Proofings

were cut from the rubber under examination, and each was impaled on a separate steel wire. They were then immersed simultaneously in a bath of water at 100° C. or of glycerol at 120° C. Each bath was regulated to ± 0.5° C. throughout the experiment, stirring of the glycerol bath being performed mechanically. At intervals, samples were withdrawn from the heating baths, plunged into cold water in order to stop the reaction and remove adhering glycerol, removed after one minute, and dried. When all the samples had been removed from the heating bath, they were placed in rotation in a plastometer oven regulated to 96° C. and given a standard factory test of 15 minutes' warm-up and three minutes between the plastometer plates. It must be observed that all times mentioned in later experi-

ments refer to time of heating in the water or glycerol baths; the eighteen minutes' heating in the plastometer oven to which each sample was subjected has not been taken into consideration. Tests were always carried out in duplicate, the results shown being the average of two separate experiments. The Y value was taken as being indicative of plasticity.

Before deciding finally on this method attempts were made to utilize an electrically controlled air oven as a means of obtaining constant heating, but repro-

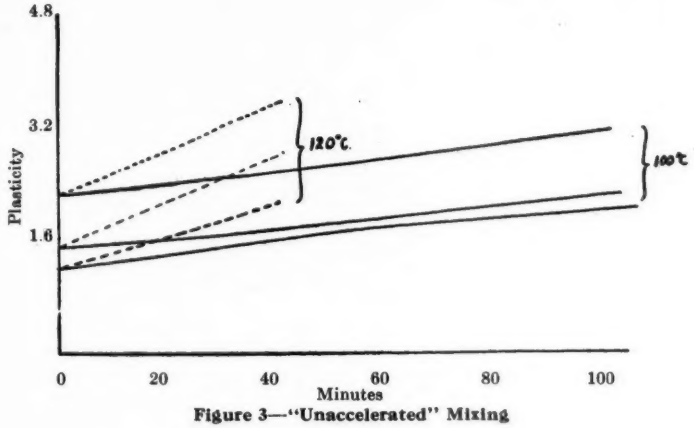

Figure 3—"Unaccelerated" Mixing

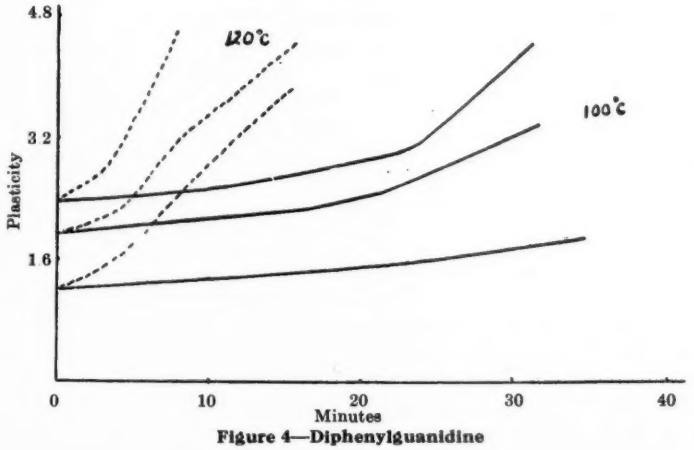

Figure 4—Diphenylguanidine

ducible results could not be obtained in this way when working at as high a temperature as 120° C. It was found that fine differences in rates of set-up could not be detected in this way, and it will be seen from Figs. 1 and 2 that the experimental error in the case of the oven-heated samples altered appreciably the relative positions of the various curves.

While carrying out rate of set-up tests on respirator tube stocks, it was observed that although results from each batch of rubber were reproducible, the rate of set-

up curves obtained from one batch did not necessarily coincide with those obtained from other batches. A similar state of affairs was evident in other mixings under examination, and as it was quite noticeable in every case that the softer batches set-up more slowly than the harder, a series of experiments were started with a view to verifying these observations. Experiments were carried out at temperatures

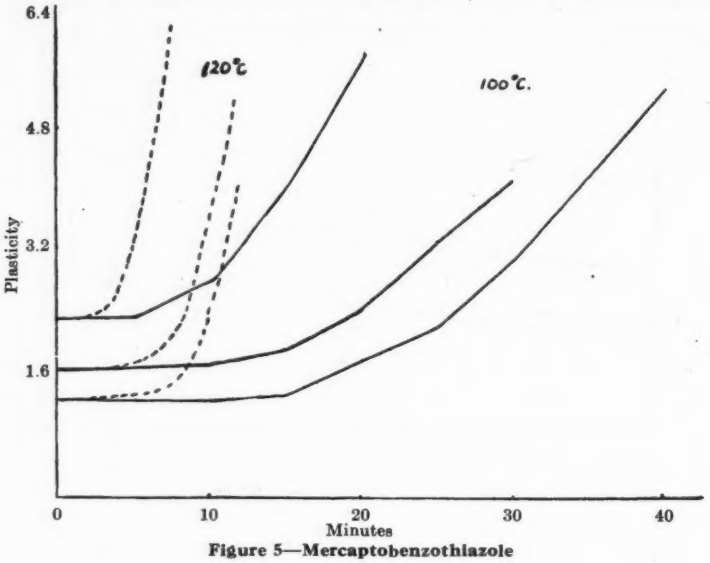

Figure 5—Mercaptobenzothiazole

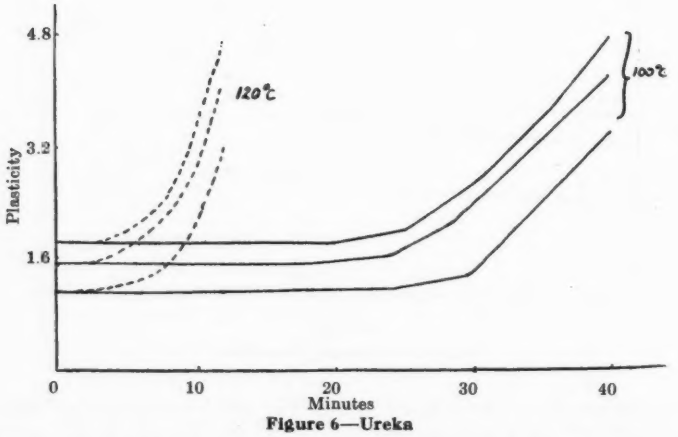

Figure 6—Ureka

of 100° C. and 120° C., and at three plasticities on stocks containing accelerators of various types and speeds, a slow, a moderately fast, a semi-ultra-, a delayed-action semi-ultra- and an ultra-accelerator being selected.

The base stock used in Experiments I to IV was: smoked sheet rubber 100, sulfur 5, zinc oxide 4, stearic acid 2, accelerator 2.

Experiment I

Accelerator, Calcined Magnesia

100° C. Time, Min.	Plasticity (1)	(2)	(3)	120° C. Time, Min.	Plasticity (1)	(2)	(3)
0	1.15	1.58	2.30	0	1.15	1.58	2.30
10	..	1.60	2.42	4	1.20	1.68	2.20
20	1.55	1.71	2.57	8	1.40	1.88	2.54
30	1.70	1.92	2.65	16	1.65	2.10	2.92
40	1.76	1.98	2.88	24	1.95	2.40	3.30
50	1.98	2.03	2.95	32	2.15	2.76	3.60
60	1.95	2.10	3.00	40	2.28	3.15	3.99
70	..	2.20	..				
80	1.97	2.30	..				
90	..	2.40	..				
100	2.10	2.51	3.55				

The results are shown in Fig. 3.

Experiment II

Accelerator, Diphenylguanidine

100° C. Time, Min.	Plasticity (1)	(2)	(3)	120° C. Time, Min.	Plasticity (1)	(2)	(3)
0	1.32	2.00	2.43	0	1.32	2.00	2.45
4	..	2.10	2.43	2	1.32	2.10	2.58
5	1.33	..	..	4	1.62	2.16	3.05
8	..	2.20	2.58	6	2.03	2.75	3.68
10	1.40	..	..	8	2.47	3.13	4.60
12	..	2.27	2.66	10	3.00	3.43	5.10
15	1.45	..	..	12	3.60	3.75	5.40
16	..	2.30	2.82	14	3.82	..	..
20	1.55	2.46	2.93	16	..	4.51	..
24	..	2.69	3.17	20	..	5.28	..
25	1.65	..	..				

The results are plotted in Fig. 4.

Experiment III

Accelerator, Mercaptobenzothiazole

100° C. Time, Min.	Plasticity (1)	(2)	(3)	120° C. Time, Min.	Plasticity (1)	(2)	(3)
0	1.27	1.70	2.36	0	1.27	1.68	2.36
5	1.27	1.75	2.36	2	1.27	1.68	2.40
10	1.27	1.75	2.80	4	1.27	1.69	2.55
15	1.35	1.95	3.97	6	1.28	1.71	3.97
20	1.80	2.48	5.88	8	1.51	1.89	6.59
25	2.25	3.36	..	10	2.08	3.40	..
30	3.13	4.15	..	12	4.26	5.38	..
35	..	..	..	14	5.85	..	..
40	5.48	5.50	..				

The above data is graphed in Fig. 5.

Experiment IV

Accelerator, Ureka (2 Parts Dinitrophenyl Ester of Benzothiazyl Disulfide Plus 3 Parts Diphenylguanidine)

100° C. Time, Min.	Plasticity (1)	(2)	(3)	120° C. Time, Min.	Plasticity (1)	(2)	(3)
0	1.15	1.55	1.80	0	1.15	1.55	1.85
5	1.15	1.60	1.81	2	1.17	1.55	1.85
10	1.15	1.60	1.80	4	1.17	1.58	1.86
15	1.15	1.60	1.80	6	1.15	1.70	1.99
20	1.15	1.60	1.81	8	1.42	2.28	2.47
25	1.20	1.75	2.04	10	2.00	3.28	3.70
30	1.43	2.35	2.65	12	3.30	4.30	4.82
35	2.39	3.10	3.56	14	..	5.40	..
40	3.51	4.40	4.89	15	5.45	..	..
50	6.15	..	..				

The results are given in Fig. 6.

In Experiment V the stock used was: smoked sheet rubber 100, zinc oxide 5, stearic acid 2, accelerator 3.

EXPERIMENT V

ACCELERATOR, TETRAMETHYLTHIURAM DISULFIDE

100° C. Time, Min.	Plasticity (1)	(2)	(3)	120° C. Time, Min.	Plasticity (1)	(2)	(3)
0	1.10	1.55	2.20	0	1.10	1.55	2.20
15	1.10	1.70	2.20	4	1.20	1.55	2.25
30	1.10	1.70	2.10	8	1.13	1.57	2.40
45	1.25	1.60	2.10	12	1.20	1.68	2.55
60	1.20	1.85	2.35	16	1.26	2.10	3.10
75	1.28	1.95	2.82	20	..	2.60	3.95
90	1.40	2.10	3.00	24	1.55	3.20	4.50
105	1.40	2.30	3.40	28	..	3.70	..
120	1.55	3.00	4.20	32	1.80	..	..
				36	..	4.60	..
				40	2.50	..	..
				48	3.40	..	..

Results of Experiment are plotted on Fig. 7.

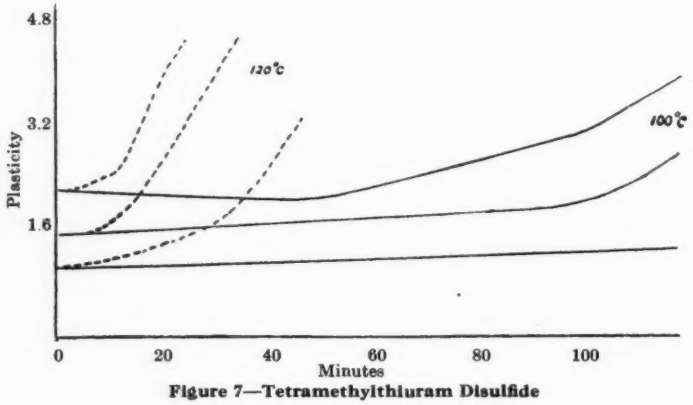

Figure 7—Tetramethylthiuram Disulfide

If these experiments are studied, it will be observed that in every case the softer rubber takes longer to set-up than the harder. For purpose of comparison a plasticity value of over 3.5 is regarded as indicating definite set-up. In Experiment I, for example, the hardest rubber with an initial plasticity of 2.30 shows set-up after 32 min. at 120° C. and 90 min. at 100° C., whereas both the softer rubbers are still quite plastic after the same times of heating (see Fig. 3). When a moderately fast accelerator such as diphenylguanidine (see Fig. 4) is used, the hardest rubber with a plasticity of 2.45 sets up after 5 min. at 120° C. or 24 min. at 100° C., whereas the softest rubber with a plasticity of 1.32 is still plastic after 8 to 10 min. heating at 120° C. and after 32 min. at 100° C. The following table (see Figs. 3 to 7) indicates the times that the softer rubbers have to be heated in order to raise their plasticity values to the initial plasticities of the hard rubbers:

Accelerator	Initial Plasticities	Time of Heating 100° C.	Time of Heating 120° C.
Calcined Magnesia	2.30	0 min.	0 min.
	1.58	80 min.	16 min.
	1.15	Over 120 min.	40 min.
Diphenylguanidine	2.43	0 min.	0 min.
	2.00	20 min.	5 min.
	1.32	Over 25 min.	8 min.
Mercaptobenzothiazole	2.36	0 min.	0 min.
	1.70	20 min.	9 min.
	1.27	25 min.	11 min.
Ureka	1.80	0 min.	0 min.
	1.55	30 min.	7 min.
	1.15	30–35 min.	8–10 min.
Tetramethylthiuram disulfide	2.20	0 min.	0 min.
	1.55	100 min.	20 min.
	1.10	Over 120 min.	32–40 min.

When a rubber with a high plasticity value is processed, it tends to set-up more quickly than a softer rubber of the same composition. The commonly accepted reason for this behavior is that the hard rubber requires the expenditure of more energy in order to break it down to a workable consistency, and this energy on being dissipated as heat causes scorching. This explanation is undoubtedly a very sound one so far as it goes, but, in addition to the danger of setting-up occurring due to the mechanical breakdown of the rubber, it has been shown that there exists as well an innate tendancy for a hard rubber to start vulcanizing more quickly than a softer one of the same composition. This acceleration of the setting-up stage, moreover, is not of negligible proportions but, as may be seen from the last table, can become a very serious factor where processing difficulties are concerned. If, therefore, rubber stocks are to be produced and processed with a minimum tendency towards scorching, especially where there is a definite trend that way, due to the composition of the mixing, it would appear to be essential to stipulate that batches when mixed should conform to plasticity standards set within very narrow limits.

Further experiments are now in hand with a view to explaining the relationship which appears to exist between mastication and rate of set-up, and it is hoped to publish the results of these supplementary experiments in the near future.

Acknowledgment

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Secondary Changes during Vulcanization of Ebonite

Part I

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All the common methods of vulcanizing rubber may be employed for the production of ebonite, but the application of some of them brings to light certain secondary phenomena, which, if not peculiar to the formation of hard rubber, are exhibited in a much more marked degree than in the case of soft rubber. In most cases the available literature is scanty, and the facts appear to be worthy of review and further investigation.

"The different modes of carrying out the process of hot vulcanization, even if performed in every case at the same temperature, produce very different results in one and the same mixing. Thus, it is very well known in practice that the methods known as dry heat curing, steam curing, press curing, hot-water curing, or curing in a sulfur bath are by no means interchangeable processes for one particular mixing." C. O. Weber (*Chemistry of India Rubber*, **1912,** p. 93) did not suggest in what respects the vulcanizates differed, but it is possible that with modern accelerated mixings the differences mentioned are much less pronounced. In the case of ebonite, however, some differences are clearly marked, whether or not an accelerator is present. There is no doubt that the differences were and are due to the incidence of various secondary changes. The present work deals mainly with such changes associated with vulcanization in steam and in water.

The Change in Weight during Vulcanization.—If a piece of high-sulfur stock is vulcanized in open steam, its weight is found to decrease, whereas a similar piece vulcanized while totally immersed in water generally increases in weight. The extent of these changes is variable, and appears to be the aggregate result of a number of factors.

A mixing consisting of rubber 100 parts and sulfur 50 parts was calendered, and samples of various thicknesses were built up from the sheet without the use of solvent. All were cut to approximately equal area of surface and weighed. They were suspended in an open steam pan so that all surfaces were exposed to the steam and heated for 3 hours at 145° C. Subsequently, the samples were found to have decreased in weight.

A duplicate set of samples was vulcanized at the same time, but completely immersed in water contained in shallow vessels placed in the vulcanizing pan. These samples increased in weight during cure, as shown in Table I.

Change in Weight on Exposure to Air.—A few hours after cure and exposure to air, both sets had diminished in weight. They were therefore conditioned by suspending them in air at room temperature for a long period. All the samples lost weight at a diminishing velocity, and after some months, each weight reached a minimum and then increased more slowly (Fig. 1).

The loss during conditioning was shown to result from a loss of water larger than the accompanying increase in weight due to oxidation. On conditioning a sample

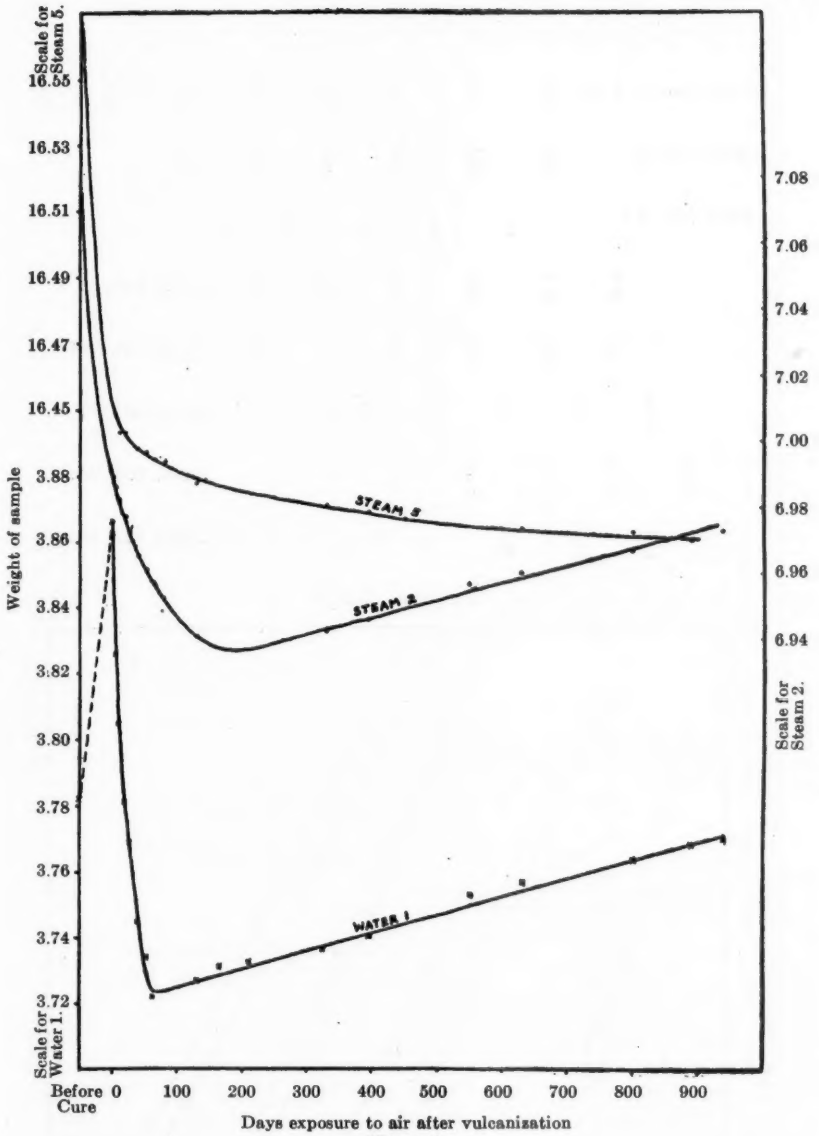

Figure 1

in a closed vessel originally containing dry air, anhydrous copper sulfate exposed to the same air clearly showed the presence of moisture. As this drying was thought to be a surface effect, the results were expressed as loss per unit area of surface (see Table 1).

The increase in weight which occurred later was apparently due to oxidation.

SCALE FOR S1 & W1	SCALE FOR S2	SCALE FOR W2	SCALE FOR S3	SCALE FOR W3	SCALE FOR S4	SCALE FOR W4	SCALE FOR W5
3·78							
3·77							
3·76	6·98						
		7·58					
3·75	6·97		8·53	8·65			
		7·57					
3·74	6·96		8·52	·64			
		7·56			12·54		
3·73	6·95		8·51	8·63		11·99	
		7·55			12·53		
3·72	6·94		8·50	8·62		11·98	
		7·54			12·52		17·96
3·71	6·93		8·49	8·61		11·97	
					12·51		17·95
			8·48	8·60		11·96	
					12·50		17·94
						11·95	

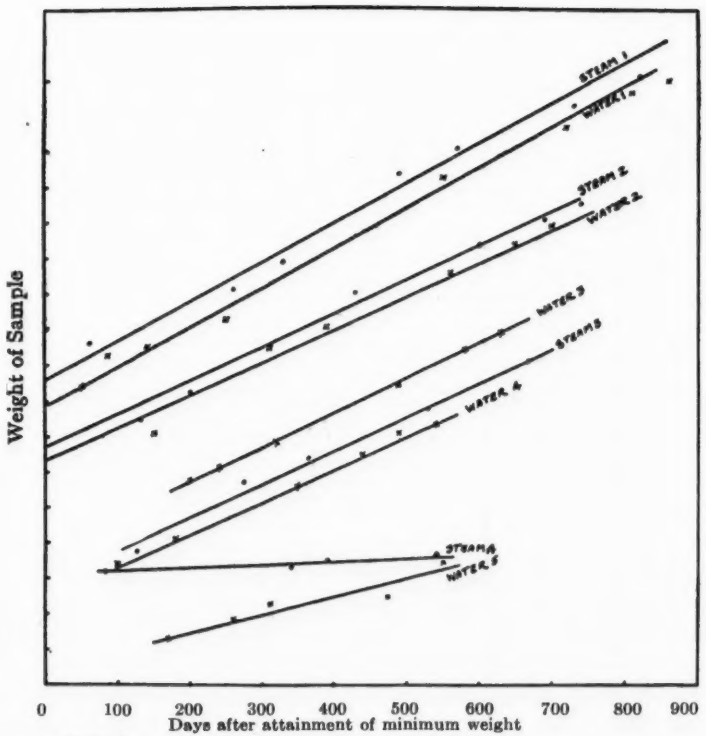

Figure 2

TABLE I

Sample	Original			Immediately after Cure			After Attainment of Minimum Weight			
	Weight (G.)	Thickness (Cm.)	Surface Area (Sq. Cm.)	Weight (G.)	Change in Weight (G.)	Change per Unit Area (G. per Sq. Cm.)	Time (Days)	Weight (G.)	Loss of Weight (G.)	Loss per Unit Area (G. per Sq. Cm.)
Steam 1	3.8446	0.116	62.5	3.7696	−0.0750	−0.00120	66	3.7192	0.0504	0.000805
Steam 2	7.0755	0.223	58.9	6.9900	−0.0855	−0.00145	200	6.9385	0.0515	0.000875
Steam 3	8.6430	0.259	65.7	8.5200	−0.1230	−0.00187	275	8.4785	0.0415	0.000625
Steam 4	12.6554	0.377	68.3	12.5444	−0.1110	−0.00162	550	12.5054	0.0390	0.000570
Steam 5	16.5672	0.503	71.1	16.4430	−0.1242	−0.00175	1090	16.4070	0.0360	0.000506
Steam 6	25.4161	0.758	76.7	25.2774	−0.1387	−0.00181	..	.....	.....	.....
Water 1	3.7821	0.114	62.55	3.8662	+0.0841	+0.00135	80	3.7208	0.1454	0.00232
Water 2	7.5912	0.225	58.95	7.7072	+0.1160	+0.00197	240	7.5250	0.1822	0.00309
Water 3	8.6326	0.261	65.7	8.7726	+0.1400	+0.00213	310	8.5760	0.1966	0.00299
Water 4	12.0015	0.360	67.9	12.1440	+0.1425	+0.00210	450	11.9288	0.2152	0.00316
Water 5	17.9776	0.535	71.8	18.1360	+0.1594	+0.00222	630	17.8951	0.2409	0.00336
Water 6	26.0681	0.764	76.8	26.2430	+0.1749	+0.00228	880	25.9665	0.2765	0.00360

TABLE II

Sample Number		Weight of Sample after Exposure to Air for the Stated Number of Days after Having Reached a Minimum Weight							
Steam 1	Days	15	60	260	330	490	570	730	820
	Weight	3.7224	3.7330	3.7408	3.7446	3.7570	3.7604	3.7666	3.7706
Steam 2	Days	130	200	350	430	600	690	740	...
	Weight	6.9423	6.9462	6.9574	6.9602	6.9668	6.9704	6.9728	...
Steam 3	Days	125	275	365	530	615	665	...	...
	Weight	8.4836	8.4938	8.4970	8.5040	8.5082	8.5107	...	..
Steam 4	Days	80	340	390	540	...	...	...	...
	Weight	12.5060	12.5068	12.5076	12.5084	...	...	...	...
Water 1	Days	50	85	140	250	550	720	810	860
	Weight	3.7270	3.7314	3.7326	3.7364	3.7566	3.7635	3.7682	3.7700
Water 2	Days	150	310	390	560	650	700	...	...
	Weight	7.5454	7.5578	7.5606	7.5680	7.5720	7.5746	...	...
Water 3	Days	90	240	320	490	580	630	...	...
	Weight	8.6020	8.6158	8.6194	8.6272	8.6322	8.6348	...	...
Water 4	Days	100	180	350	440	490	540	...	...
	Weight	11.9620	11.9657	11.9730	11.9778	11.9809	11.9819	...	...
Water 5	Days	170	260	310	475	550	...	...	...
	Weight	17.9368	17.9392	17.9414	17.9422	17.9484	...	...	...

The graph relating this increase with time of exposure to air was linear (see Table II and Fig. 2), indicating that the rate of increase of weight of a given sample was constant at least for periods up to about 3 years. It was noticed that deviations corresponded to seasonal variations of temperature and humidity.

This slow increase in weight must have been proceeding during the part of the conditioning period when the sample actually lost weight due to the more rapid loss by drying. It is therefore possible to calculate the actual weight of the dry sample immediately it was vulcanized (see Table III). In the last column of the table are shown the calculated values for the loss of weight sustained during vulcanization expressed on the basis of unit area of surface. There is an obvious tendency for the figure to increase with increasing volume in both cases, showing that the loss during vulcanization is not purely a surface phenomenon.

The Loss during Vulcanization.—The corrected figures demonstrate that, after allowing for water absorbed during vulcanization and for oxidation during drying the amount of material lost by the samples during cure was considerable. This material must include water-soluble and steam-volatile components, as well as such substances as may be produced by thermal decomposition, hydrolysis, sulfur combination, etc.

A sample of the stock was vulcanized in glass apparatus so that the volatile products could be collected for examination. Steam at atmospheric pressure and superheated to 150° C. was passed into a flask in which the sample was suspended. A hot-air bath was provided and the thermometer bulb was immediately adjacent to the sample. The outlet steam was passed through a glass condenser and the condensate was collected in a distilling flask attached to the lower end. The side tube of the receiver was connected to a pair of wash bottles containing lead acetate solution, to absorb hydrogen sulfide and thus effect a separation from the condensable portion of the products.

TABLE III

Sample Number	Minimum Weight after Conditioning (G.)	Time to Reach Minimum Weight (Days)	Increase Due to Oxidation (G.)	Calculated Weight after Vulcanization (G.)	Loss in Weight during Vulcanization	
					Calculated Loss (G.)	Calcd. Loss per Unit Area (G. per Sq. Cm.)
Steam 1	3.7192	66	0.0039	3.7153	0.1293	0.00207
Steam 2	6.9385	200	0.0120	6.9265	0.1490	0.00253
Steam 3	8.4785	275	0.0165	8.4620	0.1810	0.00275
Steam 4	12.5054	550	0.0330	12.4724	0.1830	0.00272
Steam 5	16.4070	1090	0.0654	16.3416	0.2256	0.00316
Water 1	3.7208	80	0.0048	3.7160	0.0661	0.00106
Water 2	7.5250	240	0.0144	7.5106	0.0806	0.00137
Water 3	8.5760	310	0.0186	8.5574	0.0752	0.00115
Water 4	11.9288	450	0.0280	11.9008	0.1007	0.00148
Water 5	17.8951	630	0.0378	17.8573	0.1203	0.00168
Water 6	25.9665	880	0.0528	25.9137	0.1544	0.00201

A few minutes after the commencement, pale yellow particles were noticed in the condensate. The quantity of these increased for about 35 minutes, after which their production proceeded more slowly. After 40 minutes, traces of lead sulfide were visible in the first wash-bottle, and after a further 10 minutes the formation of the yellow substance had apparently ceased and the deposit of lead sulfide was definite. The heating was then stopped, some air blown through the apparatus to sweep residual gas into the wash-bottles, and the sample removed. The rubber

was cooled and weighed in air at intervals and was found to reach minimum weight after 2 days.

The yellow solid appeared to be sulfur partly in the colloidal condition. After standing 24 hours it had coagulated and was filtered, dried, and weighed in a Gooch crucible. The contents of the crucible were then treated with bromine water and the amount of sulfur estimated by precipitation as barium sulfate.

The aqueous filtrate was neutral to litmus and showed no reactions for sulfites or sulfates, but on oxidation showed a slight positive test indicating the presence in the condensate of some soluble sulfur compound, probably hydrogen sulfide.

The lead sulfide was removed by filtration, washed, and dried to a constant weight.

As an example, the following results were obtained in one experiment.

A sample weighing 4.7956 g. suffered a loss of 0.1840 g., and yielded as product a yellow solid filtered from the condensate weighing 0.1530 g. This on oxidation and precipitation yielded 1.0828 g. of barium sulfate, which is equivalent to 0.1487 g. of sulfur. It may be concluded, therefore, that the yellow solid was almost entirely free sulfur.

Oxidation of the aqueous condensate yielded 0.014 g. of barium sulfate, corresponding to 0.0020 g. of hydrogen sulfide. Lead sulfide collected in the wash-bottles weighed 0.017 g., which is equivalent to 0.0024 g. of hydrogen sulfide.

The products collected, therefore, amounted to 0.1487 g. of free sulfur and 0.0044 g. of hydrogen sulfide, *i. e.*, a total of 0.1531 g. of material which may be taken to have emanated from the sample. Consequently, there was a loss of 0.0309 g. still unexplained. Similar results were repeatedly obtained, showing that during the vulcanization of ebonite in open steam a substantial quantity of sulfur was lost (in the above example a quantity exceeding 9 per cent of the sulfur in the sample) and a smaller quantity of hydrogen sulfide liberated, but the loss of weight of the sample was not entirely accounted for by the sum of these quantities. The balance yet to be explained is referred to below as the deficiency.

The Loss of Sulfur.—The above-mentioned loss of sulfur is compatible with observations of other workers. Thus Twiss (*Trans. Inst. Rubber Ind.*, **3**, 386 (1928)) noted that incrustations of sulfur sometimes form on dry-heat vulcanizers, indicating that sulfur vapor appears in the heating medium. Also Glancy, Wright, and Oon (*Ind. Eng. Chem.*, **18**, 73 (1926)) reported that ebonite stocks cured in the press suffered a loss of sulfur during vulcanization unless an organic accelerator was present.

It is noteworthy that in all cases the sulfur was set free during the early stages, and apparently ceased as soon as the hydrogen sulfide was evolved. The liberation of free sulfur in this way might be explained on the basis of the large quantity present during the early part of the heating period, together with the observed volatility of sulfur in steam, confirmed by conducting a control experiment using sulfur alone. This experiment is described later.

On the other hand, sulfur oxidizes readily on heating in the presence of oxygen. The steam pan is full of air at the commencement of a run, and oxygen or air is also present in the rubber in the form of minute bubbles. It would be reasonable to expect, therefore, a certain amount of oxidation which would involve a loss of free sulfur. The absence of acidity in the condensate has been repeatedly observed both in experimental and factory plants. This absence, however, by no means proves that no oxidation occurs.

If sulfur dioxide were produced, its failure to appear among the volatile products might be understood if it could be shown that subsequent reduction occurs. Such reduction is possible in various ways. First, the hydrogen sulfide produced from

the vulcanization process or otherwise may reduce the oxide with liberation of sulfur. Alternatively there may be reduction by other substances present.

The possibilities appear to be (*a*) formation of hydrogen by reaction between steam and iron, (*b*) dissociation of steam, possibly aided by catalytic action of iron oxide, and (*c*) liberation of reducing substances from the rubber.

The origin of the reducing agent was demonstrated by the following experiment. Five cc. of dilute neutral solution of potassium permanganate were introduced into each of a number of glass tubes. Samples as stated below were then suspended inside and the tubes sealed. They were supported in a vertical position in the steam pan and heated for 1 hour at 150° C. After cooling, each tube was cut and the permanganate solution acidified and titrated with ferrous ammonium sulfate.

Tube No.	Sample		Cc of Iron Solution Required	Remarks
1	None		5.8	Unchanged
2	Clean iron wire	Suspended in vapor space above the the solution	5.5	Slight brown precipitate
3	Iron rust*		5.7	Slight brown precipitate
4	Pale crepe		5.2	Definite precipitate. Partial decolorization
5	Smoked sheet		4.6	Considerable precipitate and decolorization
6	Masticated crepe		4.3	Much precipitate and decolorization
7	Clean iron wire	Immersed in the solution	0	Complete decolorization
8	Iron rust*		...	Slight brown precipitate
9	Pale crepe		0	Complete reduction
10	Smoked sheet		0	Complete reduction

* "Scale" removed from the interior of a factory steam pan.

It is clear that reduction occurred when raw rubber was present in the vapor, indicating that a volatile substance from the rubber was responsible. There were also signs of reduction due to the presence of iron. When suspended in the solution complete reduction occurred. It seems, therefore, that under vulcanizing conditions of temperature and pressure, iron reacts with water, giving rise to nascent hydrogen which is capable of reducing potassium permanganate. The limited reduction which occurred when iron was suspended above the liquid level indicated only that molecular hydrogen cannot reduce this reagent, or that the latter was not in contact with nascent hydrogen except perhaps at the surface.

Reduction by nascent hydrogen originating from this action could not possibly occur when vulcanization was carried out in glass apparatus, and the absence of acidity in this case suggests that if sulfur dioxide were formed and subsequently reduced, the latter change was brought about by reaction either with reducing substances in the rubber or with hydrogen sulfide.

It was observed that the evolution of hydrogen sulfide was negligible during the first part of the heating process and also that the liberation of sulfur ceased when the lead sulfide commenced to form. This delay in the appearance of lead sulfide is no doubt caused partly by the solubility of the gas in the condensed water. Also the amount of hydrogen sulfide available during soft rubber vulcanization is known to be exceedingly small, but a further contributory cause is possible. If, during the first few minutes of heating, the small quantity of hydrogen sulfide reacted with sulfur dioxide, sulfur would be set free and no acidity would be found in the condensate. Subsequently, of course, no further oxygen would be available in the pan.

To elucidate the point, advantage was taken of the fact that sulfur dioxide and hydrogen sulfide will not react together unless liquid water is present, and even

when moist at 100° C. they deposit sulfur only on cooling (J. Newton Friend, *Textbook of Inorganic Chemistry*, VII, 2, 115). A small pan containing sulfur was suspended inside a flask enclosed in an air bath. Steam was passed into the flask while its temperature was raised during 30 minutes to 130° C. and held at that temperature for a further 60 minutes. The outlet steam was passed through a lagged tube to a boiling dilute solution of barium chloride. Subsequently the steam was condensed and collected in a receiver connected by a side-tube to wash-bottles containing lead acetate solution.

During the 90 minutes' heating no sign of white turbidity could be observed in the barium salt. A deposit of sulfur commenced to form in the receiver when the temperature reached 120° C. and continued until a definite layer of very finely divided sulfur was formed on the surface of the water. After about 1 hour, lead sulfide commenced to appear in the wash-bottles and continued throughout. A blank experiment showed that the corks and rubber connections introduced no detectable error.

It was concluded, therefore, that sulfur reacts with steam, giving rise to a small quantity of hydrogen sulfide, but that the other reaction product is not a compound which forms a white insoluble barium salt.

Therefore the inference is that sulfur is steam-volatile and mainly distils directly from the surface of the rubber. After the surface layer has been denuded of free sulfur, the velocity of distillation depends of course upon the rate of diffusion of sulfur through the rubber. Hence the liberation of sulfur falls off rapidly at an early stage of the vulcanization process.

Steam Cure		Water Cure	
Depth (Mm.)	Per Cent Free Sulfur	Depth (Mm.)	Per Cent Free Sulfur
0.11	0.17	0.11	2.71
0.48	1.03	0.30	3.70
0.68	1.58	0.54	3.76
0.84	1.88	1.00	3.83
1.21	2.06	1.99	3.96
1.50	1.99	2.53	3.94
1.70	2.06	..	..
1.96	2.14	..	..

Distribution of Sulfur.—From the figures given it is evident that in steam-cures the sulfur loss is not a simple function of the surface area of the slab, and its effect is the production of a surface layer of finite though indeterminate thickness whose sulfur content is reduced. The existence of such a surface layer was tested by machining thin layers from a slab of ebonite which had been vulcanized in open steam. The dust was collected from each layer, sieved to pass 120 mesh and the free and combined sulfur values determined. The amounts of free sulfur were plotted against distance from the surface in Fig. 3. They show that free sulfur was lost from the surface layers, although the combined sulfur was unaffected. The depth of the affected region was about 1 mm. Hence any samples less than 2 mm. thick are not strictly comparable with those exceeding that thickness.

In the same figure are also given the results of similar operations on a slab vulcanized in water. Obviously the loss of sulfur in this case was much smaller and the thickness of the affected layer was less.

The Mechanism of Sulfur Loss.—The mechanism of the loss of sulfur during steam vulcanization is not necessarily simple.

In view of the large volume of steam per unit area of sulfur-bearing surface and of the obviously complete removal of free sulfur from the surface of the steam-

cured sample, it may be assumed that the steam remained unsaturated with respect to sulfur vapor. The amount of sulfur available at the surface then is one of the factors determining the extent of the loss. This amount is a variable for a given stock at a fixed temperature as a result of combination with the rubber. The other controlling factor is the rate of diffusion of sulfur towards the surface.

The diffusion of a dissolved substance is dependent upon its osmotic pressure and the viscosity of the medium. The latter is very high in the case of raw rubber and increases enormously as vulcanization proceeds. It is to be expected, therefore, that diffusion of sulfur in rubber would be a slow process, its speed diminishing with time. The conditions, therefore, are complicated. Indeed in addition, the low thermal conductivity produces a temperature gradient near the surface at the time when the loss is proceeding. A further variable is the frequency of renewal of steam in the pan, whether resulting from condensation or from the opening of a vent; a matter which in practice is difficult to control.

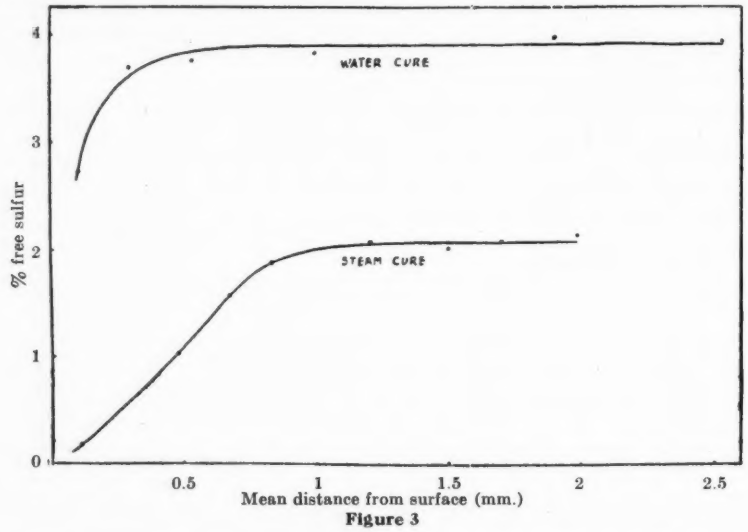

Figure 3

The mechanism of the sulfur loss, however, is made fairly clear by the experiments. The probable sequence can best be described with the aid of a hypothetical diagram (Fig. 4). Line AB represents the initial uniform distribution of sulfur. As soon as the surface becomes hot, loss of sulfur occurs. Diffusion rapidly sets in and there is a flow of sulfur towards the surface. There is thus a concentration gradient represented by OCB. But at this stage vulcanization commences from the surface and there is a cessation of volatilization, but diffusion continues (though at a diminishing speed), due to the falling concentration gradient, EDB.

At the same time sulfur-combination extends inwards, causing diminution of the amount of free sulfur at a rate which increases with time. At first, on account of the temperature gradient, the conditions are represented by a displacement of the OX axis to KL, but later they are more truly represented by displacement to HJ. The liberation of heat during hard rubber formation may well cause an excess temperature internally, with consequent increased rate of sulfur combination. In these circumstances the axis may be displaced to FG. In any case the result may be represented by a curve similar in shape to EDB where the intercept OE may be

positive or zero. In the experiment quoted, evidently the condition corresponding to HJ was reached as the combined sulfur figure was constant for the various layers. This fact can only be explained on the assumption that diffusion continues after evaporation has ceased.

The Effect of Thickness.—In thick samples whose surface area is small relative to the volume, the above process can proceed without large reduction of the internal concentration of total sulfur, but in thin samples the supply of sulfur available for migration may be limited. In the above case, for example, if the thickness had been less than 2 mm. the affected layers would have met or overlapped internally and the amount of sulfur lost would probably be less than normal. Indeed, whereas in Table III the corrected loss per unit area is seen to increase slowly with increasing volume, if the slabs were less than a certain minimum thickness it might

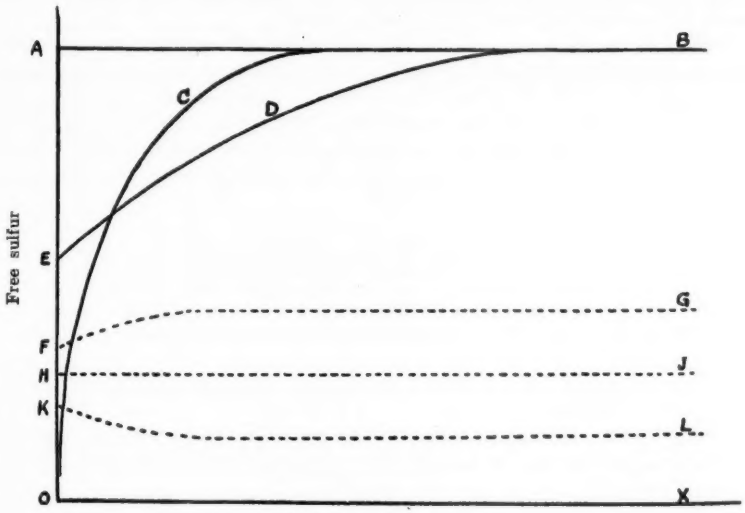

Figure 4

be expected that the loss per unit area would increase rapidly with increasing thickness. In these circumstances it is also probable that the vulcanization coefficient may be less than normal.

Vulcanization in Water.—Slabs vulcanized in water sustained a loss of weight during vulcanization which was in all cases less than that of the corresponding steam-cured samples and approximated to half the latter value.

Sulfur is insoluble in water even at vulcanizing temperatures. Nevertheless the possibility of steam distillation of sulfur may arise. An experiment showed, however, that sulfur can be heated for 1 hour in water at 150° C. in the vulcanizing pan, without weighable loss. The diminution in weight, therefore, cannot be attributed to distillation of free sulfur, although a small loss of this kind may occur during the long period of heating.

Hydrogen sulfide, on the other hand, is soluble and passes to the steam space. A part of the loss can be ascribed to evolution of hydrogen sulfide. From a consideration of the magnitude, however, it seems that loss of this gas can account for only a part of the total loss. There is, therefore, a deficiency to be explained.

The water recovered from the pans showed no sign of the presence of oxides of

sulfur. If such existed, they were lost during the boiling of the water as the pressure was released. Vulcanization in dilute barium chloride solution, however, showed that at some stage a trace of sulfate was formed. This liberation must have occurred during the early part, before hydrogen sulfide was produced.

The evolution of hydrogen sulfide during the vulcanization of hard rubber is generally attributed to substitution of sulfur in the rubber molecule, but it is evident that a secondary source is also available. If sulfur be heated under vulcanizing conditions in contact with a solution of lead acetate or potassium antimonyl tartrate, a small deposit of metallic sulfide is produced. By analogy with its action on steam, as reported above, it is reasonable to regard this as a reaction between sulfur and water with production of hydrogen sulfide which is deposited as metallic sulfide. Indeed, Cross and Higgin (*J. Chem. Soc.*, **35**, 249 (1879)) stated that sulfur begins to decompose water at 95° C. producing a trace of hydrogen sulfide. The following figures show the magnitude of the effect.

2.5 Grams of sulfur were heated with excess of potassium antimonyl tartrate solution in the vulcanizing pan at 150° C. The antimony sulfide and unchanged sulfur were removed by filtration, washed with hot water until free from soluble antimony, and the filter paper and its contents returned to the flask. Hydrochloric acid was run in and the hydrogen sulfide was led into standard iodine solution. The excess iodine was titrated with sodium thiosulfate solution and the quantity of hydrogen sulfide evolved was calculated.

During $1^1/_4$ hours heating 0.00094 g. hydrogen sulfide was evolved.
During $2^1/_4$ hours heating 0.00219 g. hydrogen sulfide was evolved.
During 3 hours heating 0.00250 g. hydrogen sulfide was evolved.
During 4 hours heating 0.00376 g. hydrogen sulfide was evolved.
During 5 hours heating 0.00468 g. hydrogen sulfide was evolved.

During the 5-hour period the rate of evolution of hydrogen sulfide was constant, and amounted to 0.0009 g. per hour.

Water Absorption.—The application of the oxidation correction, as used above, also gives corrected figures for the absorption of water by the samples during vulcanization (Table IV).

TABLE IV

Sample Number	Weight after cure (G.)	Calculated Weight after Drying (G.)	Moisture Loss (G.)	Moisture Loss (G. per Sq. Cm.)
Steam 1	3.7696	3.7153	0.0543	0.00087
Steam 2	6.9900	6.9265	0.0635	0.00109
Steam 3	8.5200	8.4620	0.0580	0.00088
Steam 4	12.5444	12.4724	0.0720	0.00105
Steam 5	16.4430	16.3416	0.1014	0.00143
Water 1	3.8662	3.7160	0.1502	0.00244
Water 2	7.7072	7.5106	0.1966	0.00334
Water 3	8.7726	8.5574	0.2152	0.00328
Water 4	12.1440	11.9008	0.2432	0.00358
Water 5	18.1360	17.8573	0.2787	0.00389
Water 6	26.2430	25.9137	0.3293	0.00429

From them it is clear that the water absorbed during open steam curing may be of some importance and that absorption from liquid water at the same temperature is 2 to 3 times as large so that it may seriously affect the product for some technical purposes. The extent of water-absorption from superheated steam was, of course, much less than that from saturated steam at the same temperature, whereas the

water-cured slabs showed an absorption figure so high that it more than balanced the losses of other substances.

The greater absorption from the liquid phase was observed as early as 1791 by Deluc (*Phil. Trans.*, **81**, 1, 389 (1791)) using whalebone, but neither he nor von Schroeder (*Z. physik. Chem.*, **45**, 109 (1903)), who also described the effect later, gave adequate explanation. It would appear that there are two equilibrium states, one for each phase.

On the other hand, Wolff and Büchner (*Z. physik. Chem.*, **89**, 271 (1915)) found that a gel, previously swollen in a liquid, did not experience a loss of absorbed substance when exposed to the carefully saturated vapor at exactly the same temperature. According to these workers, then, the smaller absorption which is normally observed is due to a difference of temperature or incomplete saturation of the vapor phase. In the present case, the steam-cured samples were suspended only about six inches above the surface of water in an open tray, the whole being centrally placed in the steam pan. In these circumstances, and in view of the need for continual circulation of steam in the pan, it is difficult to be entirely satisfied with the above view. Troubles due to the production and transport of globules of liquid water are common experience in open-steam curing, and yet it is suggested that the steam was unsaturated. There is no doubt that small differences of temperature exist in different parts of a pan, but to account for the observations, *viz.*, that absorption from steam was at most about one-half of that from water, a large temperature variation must be assumed. On the assumption that maximum absorption was attained in both cases and that the amount of substance absorbed was proportional to the vapor pressure, the difference of temperature between the steam and the water must have been no less than 20° C.

A number of workers have within recent years studied the absorption of water by rubber, and in nearly all cases the vapor has been used. On the other hand, absorption of organic liquids has been studied mainly with reference to the liquid phase.

It is significant that "drying" at room temperature and humidity is a very slow process. As shown in Table I, even the thinnest steam-cured sample required about 2 months to attain minimum weight, while the thicker slabs had not arrived at such a condition after 3 years of shelf-drying. Absorbed water lowers the dielectric resistance of an insulating material. Kemp and Malm (*Ind. Eng. Chem.*, **27**, 141 (1935)) found the value for ebonite was halved—a fact which explains the lower values frequently obtained for steam-cured than for press-cured samples of the same mixture, and also the increase to a limit which sometimes occurs on standing.

In Table IV the amounts of water absorbed are expressed as grams per square centimeter of surface, and the figures show a definite increase, indicating that water absorption depends on volume rather than on surface only.

The Rate of Oxidation.—The rates at which the samples increased in weight, apparently as a result of oxidation at room temperature and in darkness, were clearly alike for steam and water-cures of similar small thickness, but the rate was not a simple function of the area of surface. It diminished rapidly with increasing volume as shown in table at top of next page.

This suggests that the change in weight was not due to oxidation alone, but was the net result of the surface oxidation and a volume effect operating so as to produce a diminution in weight. The rate of increase in weight fell almost to zero in the case of the steam-cured slab No. 5, and the thickest slab continued to become lighter continuously for over 3 years. It was thus impossible to determine the

Sample Number	Thickness (Cm.)	Apparent Rate of Oxidation Grams per Sq. Cm. per 100 Days
Steam 1	0.116	0.0056
Steam 2	0.223	0.0046
Steam 3	0.259	0.0047
Steam 4	0.377	0.0005
Water 1	0.114	0.0057
Water 2	0.225	0.0046
Water 3	0.261	0.0049
Water 4	0.360	0.0025

(See also Fig. 5)

drying times with even moderate precision. For purposes of calculation, therefore, the figure 0.0060 gram per square centimeter per 100 days, obtained by extrapolating the curve to zero volume, was considered the correct rate of oxidation, since this eliminates the second effect.

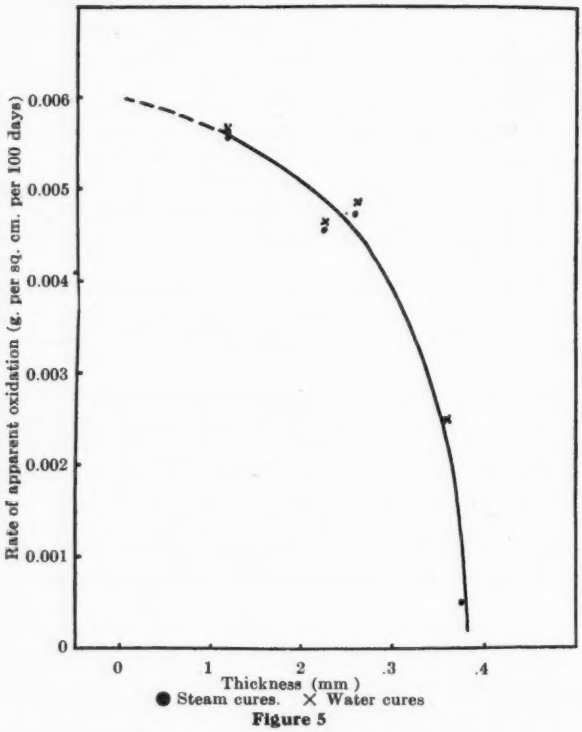

Figure 5

The nature of the volume effect is at present under investigation. It is thought that it may be connected with loss of hydrogen sulfide during storage, but whatever may be its nature, the present results show that it is independent of the mode of vulcanization of thin slabs, so far as water- and steam-heating are concerned.

It may be suggested that the fall with increasing volume may be due to increased stability of the thick samples, resulting from increased sulfur combination. As the samples were required for further work, the analysis of the whole series was deferred, but analysis of the whole of the filings from a pair of samples showed that the

coefficient of vulcanization was a little higher when the slab was vulcanized in steam—a fact which leads to the conclusion that variations in state of vulcanization in the neighborhood represented by coefficient 25, do not appreciably affect the stability towards oxygen.

	Free Sulfur (Per Cent)	Total Sulfur	Vulcanization Coefficient
Steam-cured sample	8.8	27.3	27.4
Water-cured sample	12.6	28.5	23.6

The possibility of increase of surface area by the formation of minute pores seems to be ruled out, unless it be assumed that similar changes occur in both types of vulcanizate. No visible film was formed during the aging, and no cracking was involved. Even when examined microscopically, using the Zeiss "Ultrapak" instrument, no difference of surface texture could be observed.

The Deficiency.—Latex contains a number of non-rubber substances, some of which are soluble in water and a quantity of such matter remains in pale crepe rubber despite washing. There is little doubt, therefore, that a part of the loss of weight during water-vulcanization is associated with the extraction of such substances, and thus the deficiency may be explained.

In the case of steam vulcanization the deficiency was observed, even though the steam was superheated, and this was attributed to the presence of a non-rubber substance which is volatile in steam. In an experiment quoted above it was found that potassium permanganate solution was partly reduced when rubber was suspended in the vapor space above it, and it was subsequently found that long needle-shaped crystals of a white substance were clearly visible in the upper part of such tubes.

It seems likely that a part of the material lost by solution in water was also volatile in steam. On boiling the water extract from one of the vulcanization experiments, a distinct sugar-like odor was observed. The solution appeared to differ from the extract of a sample of the crepe rubber from which it was prepared.

A slab of ebonite mix consisting of 100 parts of rubber, 50 parts of sulfur, and 20 parts of whiting (to increase the specific gravity) was immersed in water in an enamelled iron dish. A slab of pale crepe rubber of approximately similar dimensions, and weighing 125 grams was placed in a second dish, and after filling with distilled water they were heated in the steam pan for 5 hours at 150° C. The solutions were evaporated to about half their bulk and were then compared.

The extract of pale crepe rubber on cooling deposited a small amount of non-crystalline flocculent solid. There was no such deposit in the second solution.

Reduction of silver nitrate occurred much more readily in the case of the ebonite extract. There was a progressive color change to yellow, red, and brown, and, on warming, to black. The precipitate then coagulated, forming a clot of resinous material. The pale crepe rubber extract gave a brown coloration only on prolonged boiling, and would not form a mirror in the presence of ammonia.

The sodium nitroprusside test applied to the ebonite extract gave a negative result, and with ammoniacal silver nitrate a silver mirror was obtained. Further, no precipitate was obtained on addition of lead acetate solution. It is clear, therefore, that the action on silver nitrate could not be attributed to the presence of sulfur compounds, but was without doubt a reduction reaction. The solutions failed, however, to reduce Fehling's solutions and Schiff's reagent.

The color change which occurred on addition of ferric chloride also showed a difference. In this case a much deeper orange-red tint was obtained with the crepe rubber extract.

Both solutions rapidly lost their power to reduce silver nitrate on standing in daylight. Even when stored in total darkness, after 3 days no reduction occurred.

On careful evaporation to dryness, the crepe rubber extract gave a small quantity of pale brown soft resin, whereas the ebonite extract yielded a larger amount of reddish resinous matter. Both contained a trace of iron.

It may be concluded, therefore, that reducing substances were present in both cases, but that differences of behavior suggest that the two extracts were not entirely identical.

Such reducing substances have been found in raw rubber by Kirchhof (*Kautschuk*, **9**, 70 (1933)), who found also that they possess antioxidant properties. He suggested that they may be carbohydrates (sugars), but it is worthy of note that they failed to reduce Fehling's solution. Park, Carson, and Sebrell (*Ind. Eng. Chem.*, **20**, 478 (1928)) also examined the chemical changes which occurred when raw rubber was heated, and considered that the changes in the nitrogenous substances were among the most important. In view of the observation that the differences between the two extracts were not attributable to reaction with sulfur, it seems likely that these distinctions are associated with the effects of mastication.

In any event there was no difference between the rates of oxidation of the steam and water-vulcanized slabs, so that it cannot be argued that water removed an antioxidant substance unless it be conceded that such a substance is also volatile with steam.

Summary and Conclusions

(1) During the vulcanization in steam or water of sulfur-rubber mixes containing a high proportion of sulfur, there was a change of weight due to (1) loss of sulfur by volatilization, (2) loss of hydrogen sulfide, (3) absorption of moisture, (4) loss of soluble matter, (5) evolution of volatile products.

(2) Loss of sulfur from the mix was high when vulcanization was carried out in steam, and low when vulcanized in water. In the former case, it produced an outer layer of appreciable thickness which was deficient in free sulfur. This layer was, however, not visibly different from the remainder. The sulfur was lost during the earliest stages of heating, and ceased when evolution of hydrogen sulfide became appreciable. The surface loss may or may not affect the vulcanization coefficient.

(3) The mechanism of sulfur loss has been discussed. It was shown that sulfur reacts with steam or water under vulcanizing conditions, yielding a small quantity of hydrogen sulfide. The other reaction product could not be detected by the use of barium chloride in the case of steam heating, but in water some evidence of the presence of oxides of sulfur was obtained. It was concluded, therefore, that although a part of the sulfur lost probably results from successive oxidation and reduction, most of the sulfur is distilled from the surface of the sample. At the same time it was shown that water and steam, in the presence of iron, yield a reducing substance assumed to be hydrogen.

(4) Absorption of water was much larger during vulcanization in water than in steam. In both cases the period necessary to attain a minimum weight on exposure to air was very long, the time depending upon the thickness of the slab.

(5) After this period, oxidation proceeded at a velocity which was approximately constant for a given sample. This rate was therefore used to calculate the actual weight lost during vulcanization.

(6) After allowing for oxidation and for water-absorption, it was found that the loss of weight sustained during vulcanization was not a pure function of the surface area, but increased with increasing volume.

(7) The amount of water absorbed varied similarly.

(8) The rate of increase in weight of the conditioned samples was thought at first to be due to surface oxidation only, but the figures showed a declining velocity with increasing volume. It was concluded that during the oxidation process, there was a simultaneous loss, the extent of which depended on the volume of compound present.

(9) Natural aging has been studied during a period of 3 years. The speed of oxidation of thin water-cured slabs was identical with that of steam-cured samples, even though their coefficients of vulcanization were not quite identical.

(10) Among the substances removed from the rubber by hot water and by steam are reducing substances which are light-sensitive. The material removed by steam consists of a portion of that removed by water.

(11) There is reason to believe that the water-extract obtained during vulcanization is not entirely identical with that obtained from the raw material. The difference cannot be ascribed to the presence of sulfur compounds.

Further work is proceeding.

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Properties of Hard Rubber

III. Study of Surface Resistivity as Affected by Exposure to Light, Air, and Humidity

H. F. Church and H. A. Daynes

INTRODUCTION

The susceptibility of the insulation resistance of a hard rubber surface to deterioration under the influence of light, humidity and air has been known for many years and recognized as one of the outstanding deficiencies of an otherwise excellent dielectric. The work described in the present report arose from a suggestion that a convenient quantitative method was required for studying the rate of formation of acid on the hard rubber surface in relation to the composition and method of manufacture of the hard rubber, and further that simple methods of measuring the surface resistivity of large numbers of samples would be useful.

EXPERIMENTAL METHODS

Measurement of Surface Resistivity

Specific surface resistivity is defined as the resistance between two opposite sides of a square of unit area on the surface of a material after correction has been made for "volume" leakage through the body of the material. In practice the apparent surface resistivity of hard rubber may vary between 10^6 and 10^{19} ohms. The upper portion of the resistance range was covered by the rate-of-charge method with a Lindemann electrometer, the range being extended downwards by connecting low-leakage condensers in parallel with the electrometer needle. For the region below 10^8 ohms a direct deflection method was used, in which a galvanometer, a dry battery, and the sample were connected in series in a closed circuit, and the steady deflection of the needle was observed. Since the only galvanometer available was a comparatively insensitive one, the form of the later part of the time of exposure-resistance curve was not accurately investigated; it was not expected at the time that it would be of great interest. To avoid any variability due to absorption current effects in new or nearly new samples, and to ionic migration in acid films on deteriorated hard rubbers, a fixed time interval of two minutes between application of the potential and measurement of resistance was adopted. As the volume leakage current with the type of test-piece used was negligible compared with that passing over the surface, except near the beginning of the exposure before appreciable deterioration had occurred, the resistivity results were not corrected for volume leakage.

Preparation of Test-Piece

Electrodes.—Since a large number of small test-pieces had to be exposed to sunlight simultaneously and tested frequently, some form of low-capacity electrode was necessary which could be applied and handled conveniently without imposing restrictions on the size, shape, or orientation of the test-piece, and which could remain permanently in contact with the specimen without contaminating it or causing shadows or irregular reflections on the specimen. Mercury was considered deficient in these respects, and none of the usual alternative forms of electrode seemed ideal, so the use of Aquadag as a conducting paint was developed. Practical

details and experimental evidence as to its reliability have been given by Church and Daynes (*Trans. Inst. Rubber Ind.*, **6**, 82 (1930)).

Form of Test-Piece.—The samples were cut into rectangular strips 50 × 10 × 1 mm. The two Aquadag electrodes were painted along the long edges and extended 2.5 mm. across each face, leaving an exposed strip 50 × 5 mm. along the center of each large face. A leading wire was passed through a small hole within each electrode, folded back into a loop, and tightened by twisting on itself. The loops were painted over with Aquadag to ensure good contact with the electrode. This form of test-piece had the advantages that it was small and light, and was therefore easy to fit into the exposure tubes (described below) and to insulate from its supports, that the "volume" leakage correction was very small after deterioration had started, and was readily calculated when required, and that the surface leakage current for a given resistivity was high, the resistance of one face being only about one-tenth of the specific surface resistivity.

Method of Exposure and Humidity Control

Each test-piece was enclosed during exposure in a separate glass tube in which the air was maintained at a definite humidity, and its resistance was measured with-

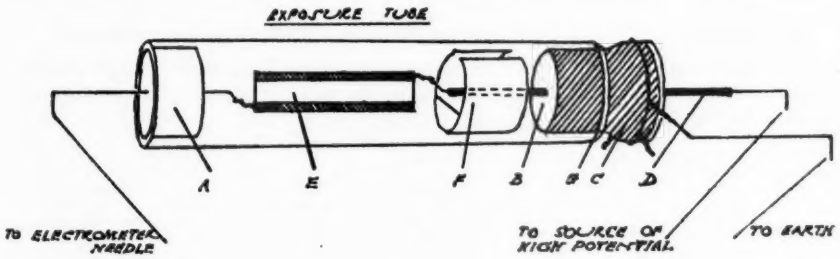

Figure 1

out removing it from the tube. An exposure tube is illustrated in Fig. 1. The tube, 15 cm. in length and 2 cm. in external diameter, was made of Lamplough's patent glass (known in sheet form as Vitaglass), in order to permit transmission of ultra-violet radiation. The wall thickness varied between 1 and 2 mm. in different tubes. One end of the tube was closed by a paraffin wax plug *A*, and the other end by a cork *B* which had been soaked in hot paraffin wax. This cork was covered with tin foil *C*, except at the ends, and was pierced by a thin ebonite tube *D* to take the leading wire. The cork was inserted so that it was isolated from the glass by the tin foil.

The sample was cut to the dimensions stated above, thoroughly sandpapered, and wiped with a clean silk cloth. After this the surface was touched no more with the fingers, and subsequent operations were carried out in a darkened room. The tinned copper leading wires were attached and Aquadag, diluted with about 6 times its volume of water, applied to form the electrodes. When the Aquadag was dry, the sample *E* was suspended within the tube by means of its leading wires, one passing through the paraffin plug, and the other through the ebonite tube in the waxed cork.

The humidity of the air within the tube was controlled by the presence of a moistened salt, or other suitable substance contained in an aluminum boat *F* inside the tube. This boat was removable so that the humidity could be easily changed, if

desired, by substitution of another boat containing a different salt. The humidity controlling substances used were dry phosphorus pentoxide 0% relative humidity (R.H.), wet sodium chloride 75% R.H., wet potassium chloride 85% R.H., wet potassium sulfate 97% R.H., water 100% R.H. After inserting the boat the tube was sealed by paraffin wax at *G*.

For the purpose of resistance measurement, the lead passing through the wax plug was connected directly to the needle of the electrometer, and the lead passing through the cork was connected to the source of high potential when required. The tinfoil on the cork was earthed, and acted as a guard ring to prevent leakage from the high potential lead to the electrometer needle by way of the cork, glass tube, and wax plug. In the later experiments, on the suggestion of D. W. Dye, an earthed screen was wrapped round the end of the tube containing the waxed plug as a protection against induced charges. The three leads were amalgamated and connected to the measuring apparatus through mercury cups. Since electrical charges were developed by friction in the processes of sandpapering, wiping, and applying Aquadag, the samples had to be left for some hours before measurements of resistance could be made. During exposure the tubes were held at each end by spring clips on a board constructed to hold several tubes and to be placed at a suitable inclination (usually 60° to the horizontal) for exposure to daylight in the open air.

PRELIMINARY TESTS ON THE EFFECTS OF SOME CONDITIONS OF EXPOSURE

Two commercial samples of hard rubber were used for these tests, a high quality sample A and a low quality sample B. The results of analysis of these samples are given in Table I.

TABLE I

Sample	Specific Gravity	Ash at 650° C., %	Organic Acetone Extract,[a] %	Free Sulfur, %	Total Sulfur, %	Combined Sulfur by Difference, %
A	1.175	1.1	1.2	2.1	32.5	30.4
B	1.389	23.5	5.0	0.8	18.1	17.3

[a] Organic acetone extract = acetone extract, less free sulfur.

Five specimens of each quality were prepared and enclosed in exposure tubes, two at 0% R.H., and the remainder at 75% R.H. Except during the period of exposure the samples were stored or tested in a darkened room. In the case of quality A, one specimen was left polished, as received from the maker, and exposed to north light at 75% R.H. for comparison with one of the sandpapered specimens exposed under similar conditions.

The glass tubes were selected to be approximately the same thickness (about 1.2 mm.) in all cases except one. This one specimen, of quality B, was enclosed in a tube of wall thickness about 2.2 mm. and exposed to north light at 75% R.H. for comparison with another of the specimens of this material exposed under similar conditions of light and humidity in the thinner-walled tubes. After conditioning for two days, the initial resistance of each specimen before exposure was determined, measurements being made at 0.5, 5, 15, and 30 minutes after application of the potential of 180 volts. Most of the specimens were then exposed simultaneously on an open roof for a total period of 150 hours of bright July daylight, some to direct sunlight and the remainder to north light. One specimen of each quality was kept in the dark as a control. Specimens in atmospheres at 75% R.H. could not be exposed to direct sunlight, since such exposure disturbed the humidity conditions and caused a deposit of water on the inside of the glass tube, even when the salt it-

self was shielded from direct radiation. After exposure the samples were conditioned in the dark for a few days, their resistance measured, and their appearance noted. The humidities were then changed without further exposure to daylight, those exposed at 0% R.H. being changed to 75% R.H. and *vice versa*. After two or three days in the dark the resistances were measured again. The results are shown in Table II. The fall of resistance is represented in the last column by the logarithm of the ratio of original to final resistance. Where the initial value was not known, the figure for another similar sample was taken; the results so obtained are given in brackets.

Conclusions from Results in Table II

Some of the results shown in Table II will not be discussed fully here because later results, in which a complete time-resistance curve was obtained, give more information. It is not possible from the present tests to estimate the relative rates at which deterioration took place under various conditions. This is the case par-

TABLE II

Sample	Original Resistivity, Ohms 0% R.H. / 75% R.H.	Exposure Conditions Light, % R.H.	Appearance after 150 Hours' Exposure	Final Resistivity, Ohms 0% R.H. / 75% R.H.	$\log_{10}$ Initial 0% R.H.	$\log_{10}$ Final 75% R.H.
A1	.....	Dark	No change	.....	..	0
	$10^{17} - 10^{18}$	75		$10^{17} - 10^{18}$		
A2	.....	N.L.	Surface very damp	1.0×10^{13}	(5.0)	
	$10^{17} - 10^{18}$	75	Several large liquid drops	3×10^{6}		11.2
A3	ca. 10^{18}	N.L.	Surface slightly darker	3.4×10^{16}	1.5	
	.....	0		1×10^{7}		(10.5)
A4	ca. 10^{18}	D.S.	Surface slightly darker	4.9×10^{15}	2.3	
	.....	0		1×10^{7}		(10.5)
A5[1]	.....	N.L.	Numerous small drops	1.3×10^{13}	..	
	7×10^{13}	75	over whole exposed surface	3×10^{6}		7.4
B1	.....	Dark	No change	.....	..	
	2.0×10^{16}	75		2.4×10^{16}		−0.1
B2	.....	N.L.	One or two damp patches	2.0×10^{16}	(0.17)	
	1.5×10^{16}	75		7.7×10^{12}		3.29
B3	2.9×10^{16}	N.L.	No change	2.2×10^{16}	0.12	
	.....	0		4.6×10^{13}		(2.62)
B4	3.0×10^{16}	D.S.	No change	1.0×10^{16}	0.48	
	.....	0		2.9×10^{12}		(3.82)
B5[2]	.....	N.L.	No change	2.9×10^{16}	(0.0)	
	2.3×10^{16}	75		1.85×10^{13}		3.09

[1] Polished surface. All other specimens sandpapered.
[2] 2.2 mm. thick glass tube. All other tubes were about 1.2 mm. thick.
D.S. = direct sunlight. N.L. = north light.

ticularly with quality A, which had deteriorated so far that further exposure produced little change in resistance at 75% R.H. The following conclusions may, however, be drawn:

1. There was no detectable change in either sample in the dark during the period of 3 weeks which elapsed between the initial and final tests (A1 and B1).

2. The effect of change of humidity on the new specimens of both qualities was small (Cf. A1–2 and A3–4, B1–2 and B3–4). It was detectable with B but scarcely so with A, owing to the limited accuracy obtainable at that portion of the range at the time when the tests were made.

3. Sample B was much the more stable sample on exposure to light (A2–4, B2–

4), and for some practical applications it would still have been as satisfactory after 150 hours' exposure to north light as when freshly sandpapered (B2–3). Owing to the unknown composition of this commercial sample, it is not possible at present

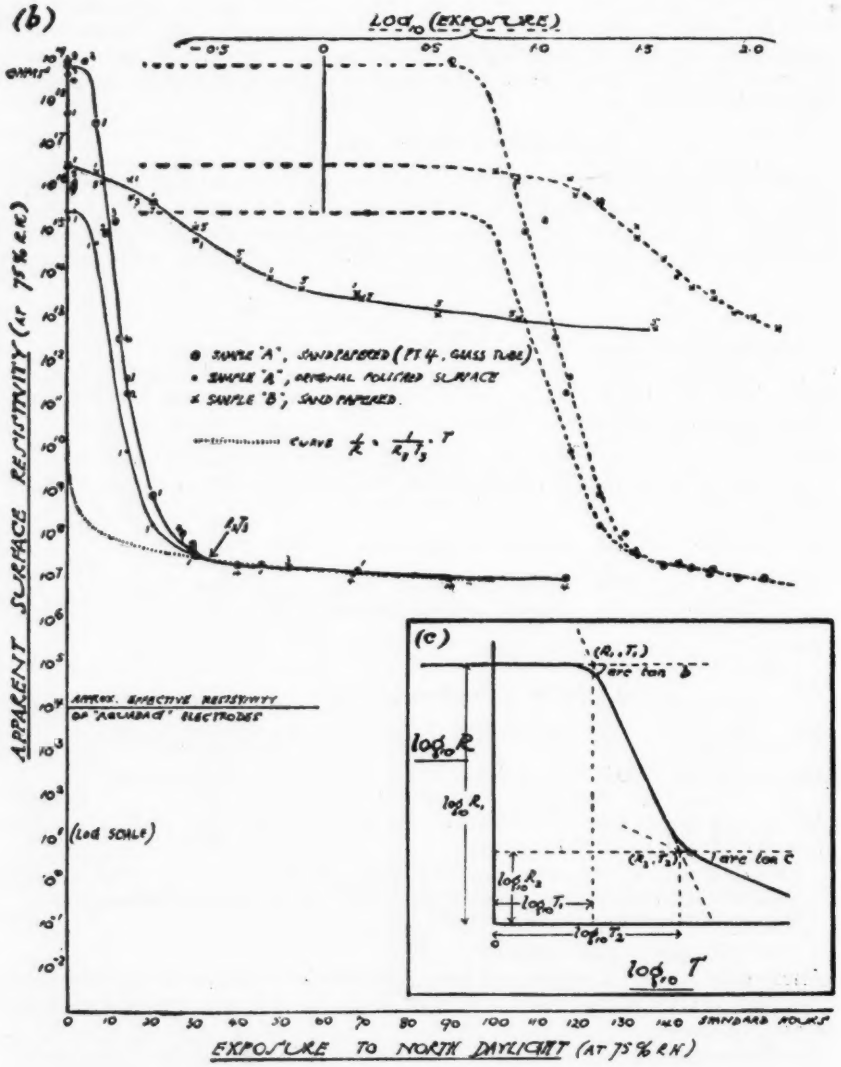

Figure 2

to give the cause of this superiority. It may be due to the intrinsic superior stability of hard rubber dust, or to the presence of mineral matter which counteracted acid formation, or to the presence of protective organic matter.

4. Although the surface resistivity of polished specimen A was initially much

lower than that of the sandpapered specimen, it reached the same final value on exposure (Cf. A2 and A5).

5. Deterioration of both qualities was more rapid in direct sunlight than in north light (Cf. A3 and A4, B3 and B4), although the difference could not be detected with A measured at 75% R.H. because deterioration had reached the stage where it was little affected by further exposure. North light was chosen for future tests as causing sufficiently rapid deterioration without involving the serious practical difficulties which arise with direct sunlight.

6. Deterioration of both A and B was more rapid on exposure at 75% R.H. than at 0% R.H. (Cf. A2 and A3, B2 and B3).

7. The retardation in deterioration of B by exposure in a thicker tube was detectable but comparatively small on the logarithmic scale (Cf. B2 and B5). The variation which could occur due to the small differences in thickness of selected tubes was small compared with that caused by differences in other conditions.

8. The effect of variations in humidity on the resistivity of an exposed specimen was much greater with A than with B (Cf. A2 and B2, A3 and B3, A4 and B4).

RELATION BETWEEN SURFACE RESISTIVITY AND TIME OF EXPOSURE

In this series of tests the change of resistance with time of exposure was studied. Tests were included to give information on the reproducibility of results and on the effect of absorption of light by the glass tubes. The following specimens were exposed:

(*a*) Quality A, sandpapered; three specimens with independent exposures, *i. e.*, at different times.

(*b*) Quality A, sandpapered; one specimen in ordinary soft glass tube, 1.0 mm. wall, with independent exposure.

(*c*) Quality A, polished; one specimen, exposed simultaneously with one sample of set (*a*).

(*d*) Quality B, sandpapered; two specimens, one simultaneously with (*c*) and (*a*), the other independently.

All specimens were exposed to north light in the open at 75% R.H. during exposure and measurement. In measuring the resistance of specimens B, there was some uncertainty as to the value to be recorded, since recovery took place on subsequent storage in the dark, and the resistance might rise by a factor of 10 during 2–3 weeks' storage. As a standard procedure all samples, on removal from the light, were stored one night and tested in the morning. An appreciably different curve would have been obtained for quality B if a longer interval had been adopted.

The actinic intensity of the light was determined every hour or so during exposure or more frequently if the light was very irregular, by means of a Watkins BEE exposure meter. The intensity was plotted against time and the area under the curve used to estimate the total effective exposure in standard hours. The standard hour was defined as the exposure equivalent to one hour of uniform light of such intensity as to darken the sensitive paper to the standard tint in 20 seconds. This corresponds to north light on a bright day in spring or autumn. The consistency in making a determination of intensity was of the order of 5%.

In connection with the comparison of tubes of different glasses, an attempt was made to measure the absorption of actinic light by the glass by exposing strips of blue print paper and printing-out paper simultaneously in the two tubes and in the open. Owing to the curvature and the streakiness of the glass, it was not possible to obtain quantitative results, but there appeared to be no striking difference between the glasses in this respect.

The results of the resistivity tests are shown in Fig. 2(*b*) in the form of curves connecting logarithm of apparent surface resistivity with exposure in standard hours. The numbers attached to the individual points refer to the different specimens which were exposed independently. The points marked 1 in the three curves refer to tests on samples which were exposed simultaneously, the measurements of light intensity being common to the three sets of observations.

Conclusions from Results in Figure 2(*b*)

1. As found in Section II, the initial apparent surface resistivity of B was much lower than that of A, but that of the polished specimen of A was still lower.

The extent to which the initial conductivity of the specimen may be attributed to leakage through the body of the material may be judged from the results of independent tests of the volume resistivity of one specimen of each quality at various times after application of the measuring potential. These results are shown in Table III.

TABLE III

Quality	Resistivity (Ohm Cm.) $\times 10^{-15}$ After 1	5	10	15	30 Min.
A	140	690	1200	1600	2600
B	1.7	6.2	10.8	14	20

In the specimens tested there is a depth of 1 mm. of material in parallel with the surface under test, so that, if the true surface resistivity were infinite, the apparent surface resistivity would be about 10 times the figure (after 2 minutes) shown in Table III, as was found to be the case.

2. In the case of quality A the exposure-resistivity curve could be divided into three well-defined portions.

(*a*) Induction period. During the first 5 standard hours the apparent surface resistivity remained practically constant. The data are rather scanty to support this generalization, but the conclusion is amply confirmed by later tests. Initial constancy of resistance for a short time is to be expected, since the leakage current measured is made up of the "volume" current through the body of the material, which is independent of exposure, and the surface current which is apparently smaller than the volume current at first. It is only when the true surface resistivity has fallen, as a result of exposure, to 10^{19}–10^{20} ohms that its effect can become perceptible.

(*b*) Rapid fall of resistance. From 5 to about 30 standard hours of exposure the resistance fell rapidly to a low value of 10^{7}–10^{5} ohms, approaching an approximately horizontal asymptote.

(*c*) Saturation period. After about 30 hours the resistivity continued to fall at a rate so much reduced as to appear negligible on the logarithmic scale. By about this time the surface of the specimen had become visibly wet with drops of acid.

(3) In the case of quality B, not only were the changes of resistance much less than in quality A, but also the three portions of the exposure-resistance curve were not so well defined. The following points were observed in which B differed from A.

(*a*) The resistivity of B appeared to fall slowly even in the early stages.

(*b*) The rate of fall of resistivity of B at the point of maximum slope was much less than that of A. The latter, which originally had a resistivity about 100 times greater than that of B, was inferior to B after only 8 standard hours' exposure.

(*c*) The resistivity of B was still falling slowly after 140 hours' exposure, but was then about 10^{5} times as high as the "saturation" value of A which had been reached

at about 30 hours. B, in fact, remained a tolerably good insulator long after A had become useless. At the end of the test there was no visible sign of acid.

4. The resistivity of the polished surface of A fell at about the same rate as that of the sandpapered surface, but about 3–4 hours earlier. The saturation value reached was the same in both cases.

5. The accuracy with which points derived from independent specimens and exposures fitted on a single curve was satisfactory in view of the number of variables involved in the conditions of exposure and the comparatively crude method of measuring the exposure. Since exposures were made at different times of the day and year, it appears that the photographic method of measuring light intensity is reasonably reliable as an index of the rate at which the light can produce deterioration in hard rubber over a considerable range of intensity and quality. Nevertheless, in order to eliminate variability of results due to errors in measurement of intensity it has been made a standard practice to include a control sample of known performance in each batch of specimens submitted to a single set of exposures.

6. The points (marked 4) obtained with ordinary glass tubes fitted well on the curve obtained with Vitaglass. Although more accurate investigation might show small differences between the two glasses, it appears that special glass is unnecessary for comparative work of this kind, provided that the tubes are selected for uniform thickness.

Mathematical Expression of Type of Log T/Log R Curve

In dealing with a large number of curves of such complicated form as the one under consideration, it is desirable to express them in some simple mathematical form, so that their main features may be numerically tabulated and easily compared. In this case it was found that, on plotting the logarithm of resistivity R against the logarithm of time of exposure T, the most important part (b) of the curve became linear over a wide range, as may be seen from the second (broken line) set of curves in Fig. 2(b). The portion (c) of the curve also approximated to a straight line of different slope, though the lower accuracy of measurement in the region of 10^7 ohms made the establishment of this relation less reliable. It is proposed tentatively to describe the main outlines of each curve according to the general scheme shown in Fig. 2(c) which may be described as follows:

(a) For a period T, the resistivity remains constant at a value R; or $R_1 = R_2$.

(b) From T_1 to T_2 the resistivity falls according to the relation $\log_{10} R_1 - \log_{10} R = b\,(\log_{10} T - \log_{10} T_1)$ where b is a positive constant representing the slope of the line.

Therefore
$$\frac{R}{R_1} = \left(\frac{T}{T_1}\right) - b$$

(c) During the period after T_2 the slope c of the line is much less than b but the equation is of the same type.

$$\frac{R}{R_2} = \left(\frac{T}{T_2}\right) - c$$

It should be noted that the points (R_1, T_1) and (R_2, T_2) are not points on the curve; they are convenient reference points by which to locate the pattern of three intersecting straight lines and to indicate the regions in which a transition takes place from one portion of the curve to another.

The values of the constants derived from the three curves under consideration are shown in Table IV. The slope c in the case of quality A is given as 0.8, though

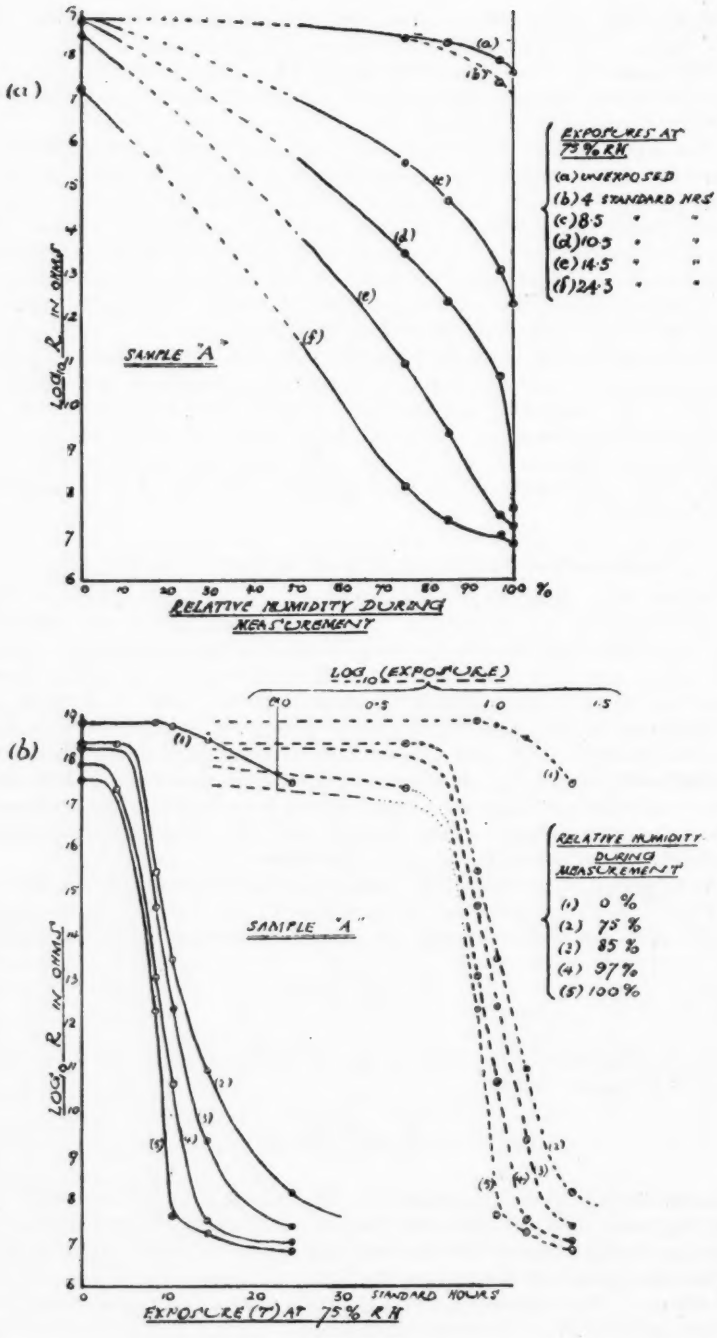
(a)
EXPOSURES AT 75% RH
(a) UNEXPOSED
(b) 4 STANDARD HRS
(c) 8·5 " "
(d) 10·3 " "
(e) 14·5 " "
(f) 24·3 " "
SAMPLE "A"
LOG10 R IN OHMS
RELATIVE HUMIDITY DURING MEASUREMENT
%
(b)
LOG10 (EXPOSURE)
RELATIVE HUMIDITY DURING MEASUREMENT
(1) 0 %
(2) 75 %
(3) 85 %
(4) 97 %
(5) 100 %
SAMPLE "A"
LOG10 R IN OHMS
EXPOSURE (T) AT 75% R H
STANDARD HOURS

Figure 3

by the graphical method of determination it could scarcely be distinguished from the value unity which has been observed in later tests with several similar specimens. The difference between 0.8 and 1.0 is small in comparison with the difference between slopes b and c, so that the estimates of R_2 and T_2 are only slightly affected by this uncertainty. In the case of quality B, owing to the slow deterioration, the "saturation" period was scarcely begun, so that no value of c could be given, but tentative values of R_2 and T_2 are indicated.

TABLE IV

Specimen	R_1 Ohms	T_1 Standard Hours	b	R_2 Ohms	T_2 Standard Hours	c
A, polished	2.8×10^{15}	5.8	13.8	3.3×10^{7}	21.4	0.8
A, sandpapered	7.1×10^{18}	5.6	17.7	3.0×10^{7}	24.6	0.8
B, sandpapered	3.2×10^{16}	11.5	4.2	1×10^{13}	79	...

The differences of behavior among the various samples may be appreciated from Table IV in the following manner. The initial resistivities are shown by the value of R_1. The superiority of the loaded specimen B after the first few hours is seen in the longer induction period T_1, the smaller slope factor b, the higher "saturation" resistivity R_2, and the longer time T_2 taken to reach the saturation stage.

The significance of the slope factor may be illustrated by calculating the times taken under various conditions for the resistivity to fall, say, 10 per cent. For example, with A, sandpapered, during rapid fall, 3 minutes; B, during rapid fall, 1.5 hours; and A, during "saturation," 10 hours.

The above analysis may be supplemented in practical applications by calculation of the time T_3 when the resistivity falls to a value R_3, which is just too low for the intended use of the material. Such a limiting value varies to some extent according to the use in view, but 10^{14} ohms may be taken as a suitable minimum value for most purposes requiring a high-grade insulator. The times required to reach 10^{14} ohms, read from the $T/\log R$ curves, were 10.5 hours for A sandpapered and 45 hours for B. Within the middle steep portion of the log $T/\log R$ curve the time for any other value of R_3 may be calculated by observing that R changes by a factor of 10 for every change of $1/b$ in the logarithm of T.

EFFECT OF HUMIDITY DURING MEASUREMENT ON RESISTIVITY AT VARIOUS STAGES OF DETERIORATION

The conclusions drawn in Section III apply only to the case where the samples are exposed in an atmosphere of 75% R.H., and are measured at the same humidity. In practice humidity varies during exposure and use, and this variation may affect both the rate of deterioration and the resistivity at any stage of deterioration, so that an instrument depending on hard rubber for insulation may behave erratically through diurnal variations of humidity besides becoming progressively worse as a result of exposure to light. To investigate this point, samples of hard rubber of qualities A and B previously described were exposed at 75% R.H. to north daylight under the standard conditions. Periodically the samples were withdrawn from exposure and their resistivities measured at 75, 85, 97, 100, 0, and 75% R.H. in order after two days' conditioning in the dark at each humidity.

In Figs. 3(a) and 4(a) families of curves show the relation between relative humidity and log R at various times of exposure T. The same data are plotted in Figs. 3(b) and 4(b) to show the relation between log R and T (or log T) at various relative humidities of measurement. Figures 3(a) and (b) refer to quality A hard rubber and 4(a) and (b) to quality B.

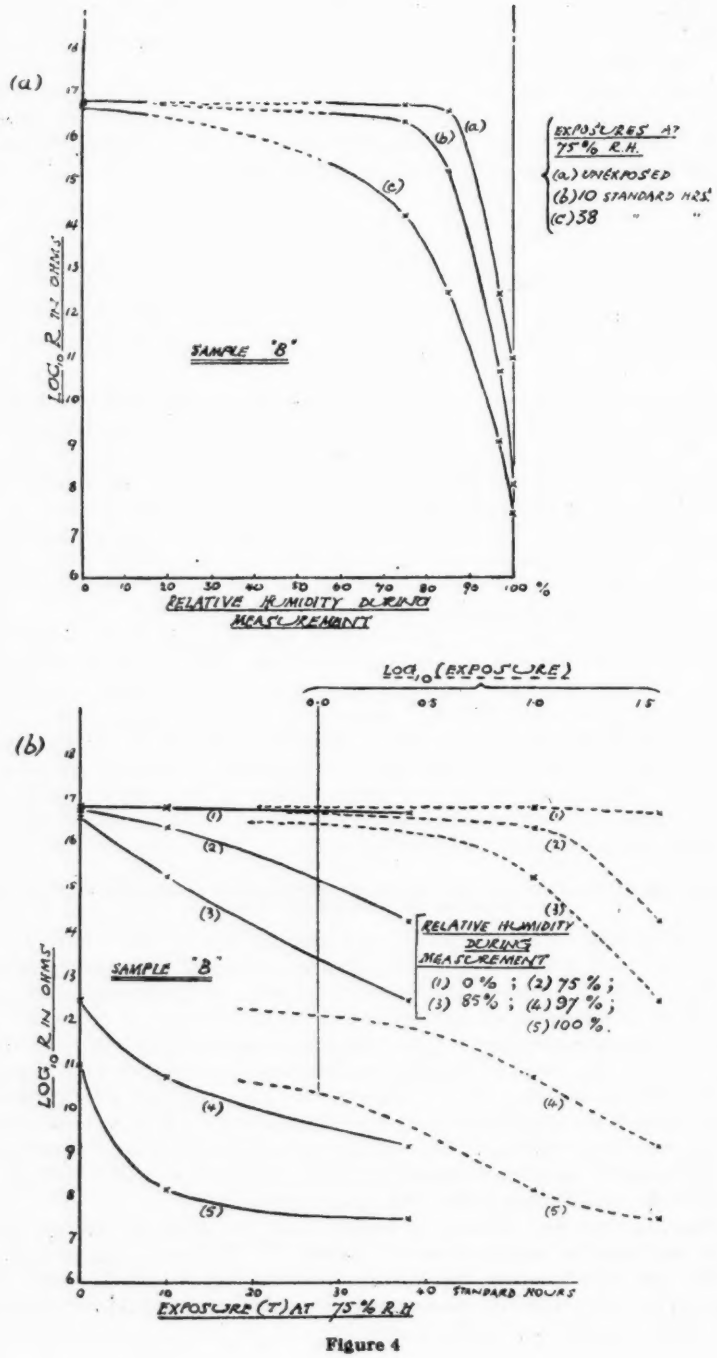
(a)
LOG10 R IN OHMS
SAMPLE "8"
RELATIVE HUMIDITY DURING MEASUREMENT
0 10 20 30 40 50 60 70 80 90 100 %
EXPOSURES AT 75% R.H.
(a) UNEXPOSED
(b) 10 STANDARD HRS.
(c) 38 " "
(b)
LOG10 (EXPOSURE)
0·0 0·5 1·0 1·5
LOG10 R IN OHMS
SAMPLE "8"
RELATIVE HUMIDITY DURING MEASUREMENT
(1) 0% ; (2) 75% ;
(3) 85% ; (4) 97% ;
(5) 100%.
0 10 20 30 40 STANDARD HOURS
EXPOSURE (T) AT 75% R.H

Figure 4

Conclusions from Figures 3–4

1. In the case of quality A, humidity had comparatively little effect on the resistivity R_1 of the new material. The same was true of quality B except at humidities above about 85% R.H. when a sharp fall occurred (by a factor about 5×10^5).

2. While observations at 75% R.H. are useful for comparing stabilities of different materials, it is clear that the constants of the log T/log R curve are greatly dependent on humidity of measurement. (*a*) The variation of R_1 has already been discussed. (*b*) With quality A the induction period T_1 decreased continuously with increase of humidity, especially between 0 and 75% R.H.; with quality B the induction period probably became negligible at high humidities; although the results shown in Fig. 4(*b*) did not contain sufficient observations at short exposures to decide the latter point, subsequent tests have shown that the resistivity measured at 97% R.H. falls by a factor of 10 in the first 1.5 hours' exposure. (*c*) The slope b for quality A was not greatly altered, except perhaps at 0% R.H., but the straight portion of the curve from which the constant was calculated was not so well defined at high humidities owing to the lack of points on the knee of the curve. The general effect was an increase of slope and possibly a decrease in definition of the end of the induction period with increasing humidity. The slope for quality B varied in a complicated manner, but was generally much less than for quality A. (*d*) T_2 and R_2 were not well defined, owing to lack of points, but in the case of quality A the former decreased with increase of humidity and R_2 probably decreased. It was impossible to obtain values for these constants with quality B. (*e*) The practical figure of merit T_s which is a composite quantity involving R_1, T_1, and b, decreased with increasing humidity in the case of quality A, this being especially marked between 0 and 75% R.H. It had no real value in the case of quality B above 94% R.H. since R_1 was then below 10^{14} ohms. If 10^{14} ohms is accepted as the practical limit, then quality B was useless above 94% humidity even when new. This disadvantage must be set against the advantage of its superior stability at 75% R.H.

3. There was a systematic difference in shape between the humidity/log R curves for qualities A and B. Thus, after 10 standard hours' exposure, measurements at 75% R.H. showed B to be much better than A, whereas at 97% R.H. they were practically equal. The tendency in quality B for the fall in resistivity to be confined to the higher humidities became less noticeable as exposure progressed, as had been noted by Curtis (U. S. Bureau of Standards *Sci. Paper*, No. **234**, 1914), but there was always a difference between A and B in this respect. In the case of quality A an opposite tendency was observed in the later exposures, the resistivity tending to become constant at about 10^7 ohms from 85 to 100% R.H. when saturation conditions were reached.

EFFECT OF HUMIDITY DURING EXPOSURE ON RATE OF DETERIORATION

Five samples each of qualities A and B were prepared and exposed under the usual conditions, but at various humidities, namely, 0, 75, 85, 97, and 100% R.H. Periodically the samples were withdrawn from the light and conditioned for 2 days at 75% R.H., so that all resistivity measurements were made under the same humidity conditions. The resistivities therefore gave an indication of the rate of formation of acid under the various conditions of exposure. The curves showing the relations between log R and both time of exposure and humidity during exposure for sample A are to be found in Figs. 5(*a*) and 5(*b*). The relative humidity/log R curves for quality B are shown in Fig. 6.

It is of interest also to consider the case of a sample exposed and measured at the

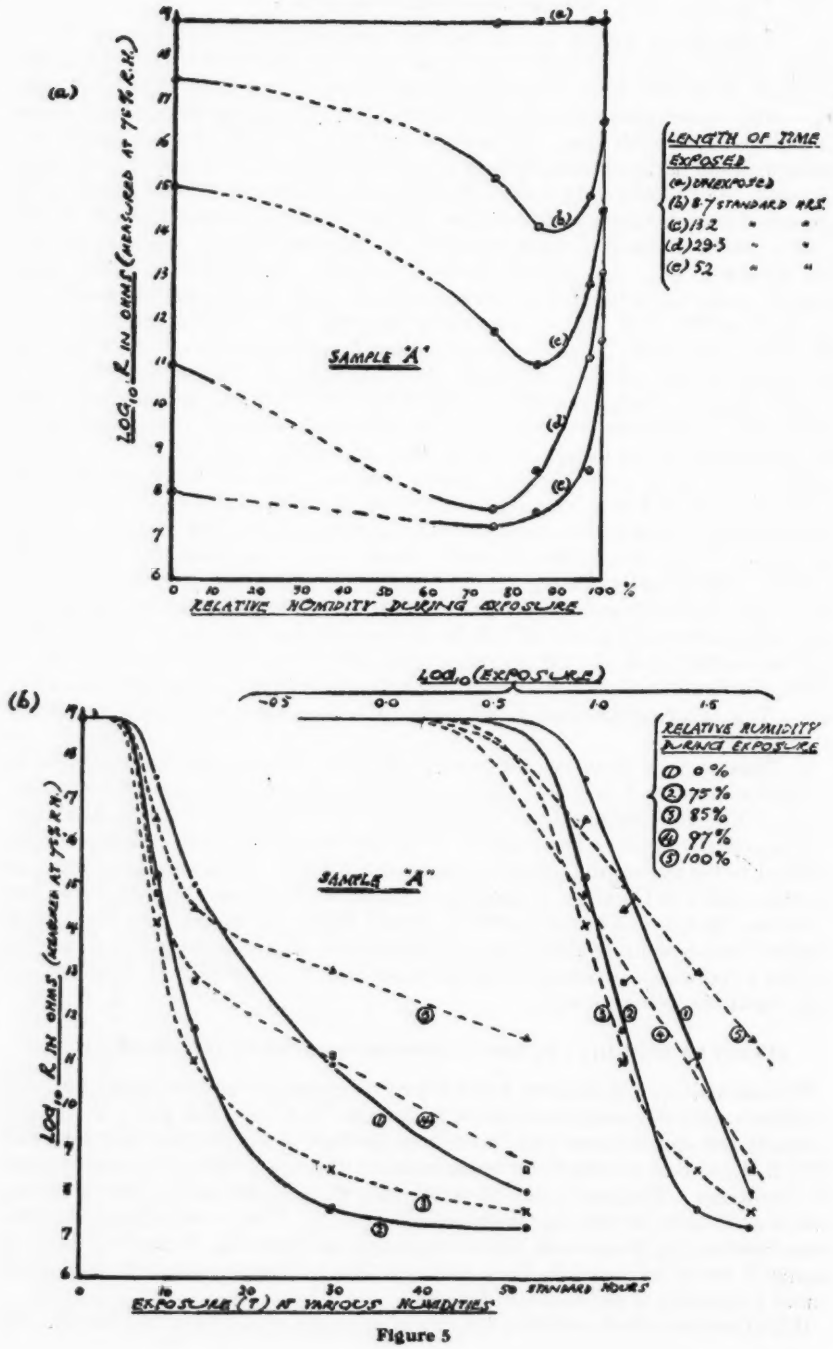
(a)
LOG10 R IN OHMS (MEASURED AT 75% R.H.)
SAMPLE "A"
RELATIVE HUMIDITY DURING EXPOSURE
%
LENGTH OF TIME EXPOSED
(a) UNEXPOSED
(b) 8·7 STANDARD HRS.
(c) 13·2 " "
(d) 29·3 " "
(e) 52 " "
(b)
LOG10 (EXPOSURE)
LOG10 R IN OHMS (MEASURED AT 75% R.H.)
SAMPLE "A"
RELATIVE HUMIDITY DURING EXPOSURE
① 0%
② 75%
③ 85%
④ 97%
⑤ 100%
EXPOSURE (T) AT VARIOUS HUMIDITIES
STANDARD HOURS

Figure 5

same humidity, and to find how the resistivity depends on both time and humidity. This corresponds to the practical case of an insulator exposed to light and used in an atmosphere of approximately constant humidity. This point has not been tested directly, but data may be derived from the results of this and the previous section on the assumption that the form of the log R/humidity of measurement curve is independent of the humidity of exposure. The method is illustrated by the following example.

From Fig. 5(b) it is found that a sample of A exposed for 12.8 standard hours at 85% R.H. had a resistivity $10^{11.0}$ ohms at 75% R.H. From Fig. 3(b) it is

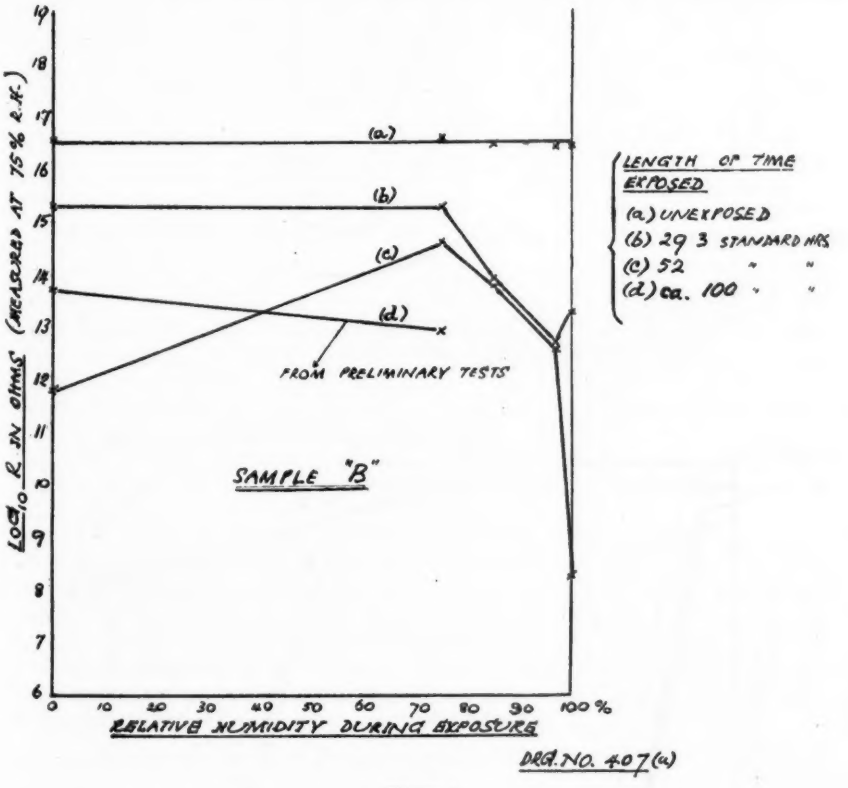

Figure 6

found that a sample of the same material exposed for 14.1 standard hours at 75% R.H. had the same resistivity, 10^{11} ohms, at 75% R.H., and $10^{9.4}$ ohms at 85% R.H. It is therefore concluded that a sample both exposed and measured at 85% R.H. would have a resistivity of $10^{9.4}$ ohms after an exposure of 12.8 standard hours. The curves in Figs. 7(a) and (b) have been constructed in this way.

Conclusions from Figures 5–7

1. In the case of quality A, tested at 75% R.H., deterioration was faster at humidities between 70 and 90% R.H. than at humidities outside that range in either direction; but the humidity at which the maximum rate occurred probably

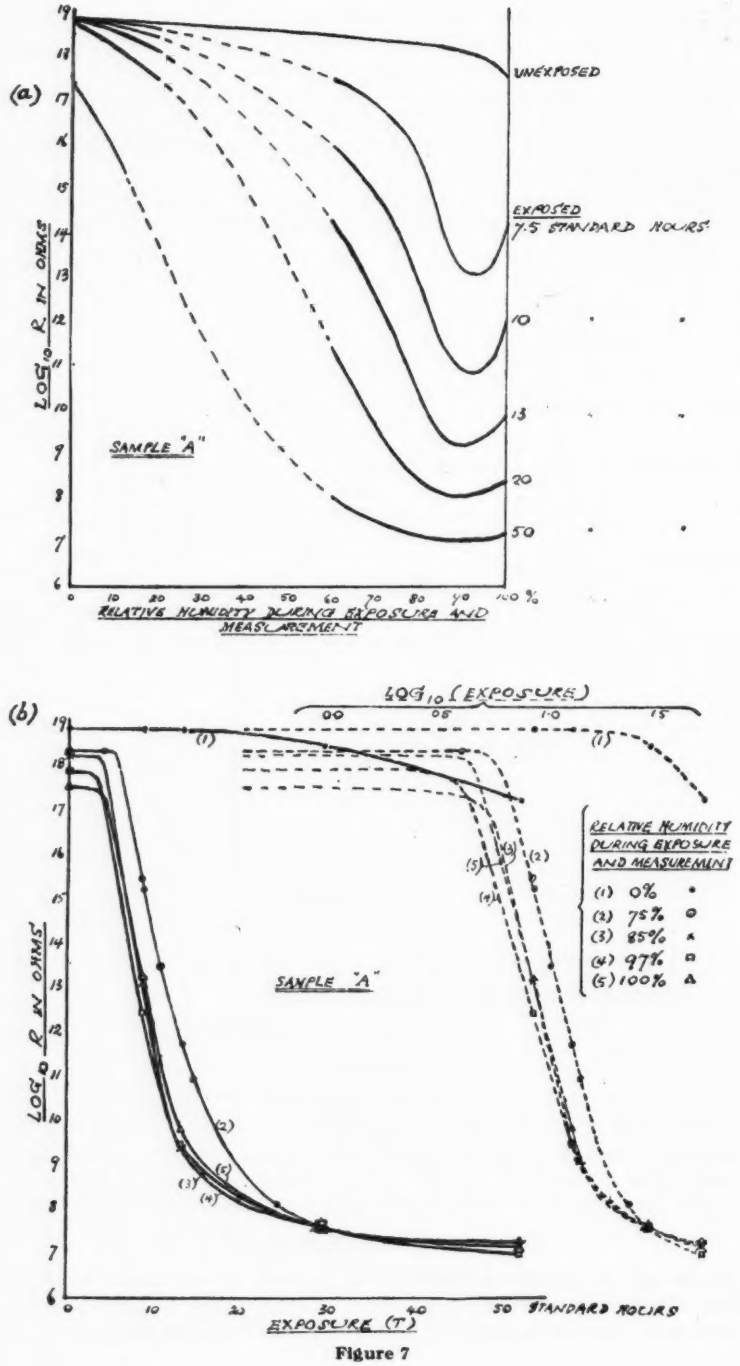
(a)
LOG10 R IN OHMS
UNEXPOSED
EXPOSED
7.5 STANDARD HOURS
10
13
20
50
SAMPLE "A"
RELATIVE HUMIDITY DURING EXPOSURE AND MEASUREMENT
(b)
LOG10 (EXPOSURE)
RELATIVE HUMIDITY DURING EXPOSURE AND MEASUREMENT
(1) 0%
(2) 75%
(3) 85%
(4) 97%
(5) 100%
SAMPLE "A"
EXPOSURE (T)
STANDARD HOURS

Figure 7

varied from 90 to 70% R.H. as deterioration proceeded. After about 50 hours' exposure, the resistivity varied little over the range 0–90% R.H., probably because the acid film had reached the "saturation" stage, at which its resistance was comparatively insensitive to further exposure. The retarding effect of the high humidities, 97 and 100% R.H., was, however, still marked. It is not possible to give accurate constants for all the log T/log R curves, because they did not conform in all cases to the standard type described in Section III, being somewhat irregular at the higher humidities, but the approximate analysis shown in Table V, in which doubtful figures are enclosed in brackets, will illustrate quantitatively the principal effects of humidity of exposure, all measurements being made at the same humidity.

TABLE V

Humidity, % R.H.	T_1 Standard Hours	b	T_2 Standard Hours	R_2 Ohms	T_s Standard Hours
0	6.6	11.9	ca. 60	ca. $10^7 - 10^8$	16
75	5.3	17.4	ca. 20	ca. $10^7 - 10^8$	10
85	4.2	15.0	ca. 20	ca. $10^9 - 10^{10}$	9
97	(2.5)	(7.6)	...	.....	10
100	(3.1)	(6.0)	...	.....	16

T_s = time to reach a selected resistivity of 10^{14} ohms.

It is seen that T_1 decreases as humidity increases, while b shows a maximum at about 75% R.H. The low rate of deterioration at 0% R.H. is shown by the high value of T_1 and the comparatively low value of b, which is reflected in the high value of T_2. The retardation at high humidities is shown by the low values of b at 97 and 100% R.H. The existence of a maximum rate of deterioration is clearly shown in the minimum value of T_s at 85% R.H. At 85% R.H. the value of R_2 is higher than is usually observed at 75% R.H.

2. In the case of quality B, no detailed analysis is possible, since the results were irregular. It was noticed that there was some difficulty in repeating results at high humidities.

3. According to the estimated curves for quality A, if the resistivity were measured at the same humidity as that during exposure, there would be practically no important difference in behavior over the range 85 to 100% R.H., but the change in resistivity would be somewhat less rapid at 75% R.H., and very slow in the dry condition. The maximum in the rate of deterioration at about 90% R.H. would be still observable, but much less marked. The following is an analysis of the log T/log R curves, which conformed well to the standard type so far as could be seen from the number of points available.

TABLE VI

Humidity, % R.H.	T_1 Standard Hours	b	T_2 Standard Hours	R_2 Ohms	T_{14} Standard Hours
0	30	..	...	....	..
75	6.0	19.2	ca. 22	ca. 10^8	10.0
85	4.8	20.0	ca. 16	ca. 10^8	8.0
97	4.1	16.7	ca. 16	ca. 10^8	7.5
100	4.9	18.0	ca. 16	ca. 10^8	8.0

RATE OF DETERIORATION IN ARTIFICIAL LIGHT

Sandpapered samples of commercial hard rubbers A and B, as described in Section II, were enclosed in the usual exposure tubes at 75% R.H., and exposed at a distance of 15 cm. from the tungsten filament of a 100-watt gas-filled lamp, the ex-

posed surfaces being directed towards the filament. The distance of 15 cm. was the smallest which could be adopted without serious heating of the tubes. Even under these conditions the tubes became slightly warm to the touch. The positions of the samples were periodically interchanged in order to eliminate the effect of any unevenness in the intensity of the light. The intensity as measured by the photographic exposure meter was about one-ninth of that defined as standard intensity. On plotting the logarithm of resistivity against the logarithm of time, it was found that the curves conformed to the standard type. In the case of quality B, exposure had to be discontinued before saturation was reached, owing to the humidity-controlling salt creeping on to the specimen. (The boat containing the salt during these tests was not of the improved type shown in Fig. 1, but was attached to the leading wire.) The values of the various constants are shown in Table VII together with the corresponding daylight exposure results from Section III.

Conclusions from Results in Table VII

1. The course of deterioration seemed to be essentially the same in artificial light as in daylight.

2. The rate of deterioration in the artificial light used was less than in bright daylight, but the relation between exposure and resistivity in the case of quality A is the same within the limits of experimental error, when exposure was expressed in

TABLE VII

Sample	Light	R_1 Ohms	T_1 Standard Hours	b	R_2 Ohms	T_2 Standard Hours	c	T_3 Standard Hours
A	Artificial	7.2×10^{18}	5.3	17.9	7.7×10^{7}	22.2	ca. 1	9.9
	Daylight	7.1×10^{18}	5.6	17.7	3.0×10^{7}	24.6	0.8	10.3
B	Artificial	4.5×10^{16}	14.5	3.25	.....	..	...	..
	Daylight	3.2×10^{16}	11.5	4.2	1×10^{13}	79	...	45

terms of standard hours as measured by a photographic meter. This suggests that the portion of the spectrum responsible for the deterioration of ebonite is substantially the same as that involved in the darkening of photographic paper, at least in the case of pure rubber-sulfur ebonites, where there are no complicating factors due to the presence of mineral ingredients, etc.

In the case of quality B, there was a small increase in T_1 and a decrease in slope b in artificial light, compared with daylight, both tending to increase the time required to reach a given resistivity. This effect, however, was not merely equivalent to an extension of the time scale, as would be the case if b were unchanged. The ratio between the time taken to reach a given resistivity with artificial light to that with daylight increased as the resistivity fell. This was probably connected with the phenomenon of recovery, which has already been mentioned in Section III in connection with quality B, and which will be further discussed in the next Section.

3. The use of artificial light for comparative tests of surface stability has obvious advantages, and is worthy of further study. The difference between qualities A and B in bright daylight was well revealed by the relative stability in artificial light, but the results suggested that in less intense, diffused light the difference might be more marked and in favor of quality B; this qualification must be borne in mind in interpreting results of accelerated light aging tests with loaded hard rubbers.

THEORETICAL DISCUSSION

Properties of Ideal Uniform Film

It is possible now to form a tentative working hypothesis as to the method of formation of the conducting surface. Consider first the ideal case of a perfect insulator covered by a uniform film of aqueous solution of sulfuric acid in equilibrium with the atmosphere.

Let x = mass of acid (anhydrous) in g. per sq. cm. of surface;
H = percentage relative humidity of the atmosphere;
C_H = concentration of acid in solution in g. per 100 g. of liquid;
D_H = density of liquid in g. per cc. at concentration C_H;
K_H = specific conductivity of the liquid in reciprocal ohm-cm.;
t = thickness of film in cm.

Then it can be shown that:

$$t = \frac{100x}{C_H D_H}$$

and the surface conductivity (reciprocal of resistivity)

$$= tK_H = \frac{100\ K_H x}{C_H D_H}$$

The relations between C_H and H, K_H, and D_H are known, and are plotted in Fig. 8. These curves may be used to calculate the conductivity as a function of humidity and quantity of acid in the ideal case. The significant data are shown in Table 8. The extreme values of 0 and 100% R.H. are excluded, since the properties in question change so rapidly near these values that conclusions based on them would be unreliable.

TABLE VIII

H	K_H	C_H	D_H	$K_H/C_H D_H$	$1/C_H D_H$
75	0.73	30	1.22	0.020	0.027
85	0.69	23	1.16	0.026	0.037
97	0.30	8	1.05	0.036	0.119

Significance of the Shape of the Log T/Log R Graph

In the following discussion an attempt is made to explain the shape of the log T/log R curve. At first sight it appears that the curve is of a typical autocatalytic form—a slow induction period corresponding to the formation of a deterioration catalyst, followed by rapid deterioration under the influence of the catalyst, with final slowing down of the reaction.

However, it is believed an alternative hypothesis is better suited to the experimental facts available, and its main terms are as follows. The fresh surface of the insulator, free from conducting impurities, has an extremely high surface resistivity. In the early stages of deterioration (the induction period) the conducting impurities are formed only as isolated spots and patches and no complete conducting paths cross the specimen, so that the measured surface resistivity changes very little. When conducting paths form, by the linking up of the impurities, the resistivity falls rapidly, until a complete surface film covers the whole surface of the insulator. After this, further increase in the conductivity of the film is proportional to the development of acid in the film, and consequently shows only as a relatively slow fall in resistivity.

This hypothesis is now examined quantitatively so far as it applies to the foregoing experimental results.

The Point (R_2, T_2) on the Log T/Log R Graph.—The rapid fall of resistivity of an unloaded hard rubber sample exposed and measured at 75% R.H. slows down somewhat abruptly at about 10^7–10^8 ohms. The resistivity at this point varies comparatively little from 5×10^7 ohms among samples differing in surface condition (sandpapered or polished) and, from later data, among samples differing in time of vulcanization or ebonite dust content. At 75% R.H., $K_H = 0.73$, so that the apparent thickness of the acid film is about 2.7×10^{-8} cm., which is within the range of values assigned to the diameters of most simple molecules.

The practical case differs in some respects from the ideal case. (1) Even in an unloaded hard rubber, the acid liquid may contain small quantities of salts formed by secondary reactions with the non-rubber components and with ammonia from the air. Sulfurous acid also has been found. These will modify the hygroscopicity and specific conductivity of the film. (2) The distribution of acid on the surface is probably not uniform, since by the time the resistivity has decreased from the value R_2 by a further factor of 10, the acid becomes visible in minute drops on the surface. Under such conditions the apparent thickness calculated from the conductivity will be less than the true mean thickness, since regions of high local thickness contribute little to the conductivity of a thin layer so long as they do not coalesce to form conducting chains from one electrode to the other. (3) It is not permissible to assume that the properties C_H, D_H, and K_H, of a film one molecule, or even a few molecules, thick are precisely the same as for greater thickness in equilibrium with the same relative humidity.

In spite of these sources of uncertainty, the fact that the abrupt fall in resistivity, covering a range of a billion to 1, slows down sharply when the resistivity reaches a value (5×10^7 ohms) of about the magnitude expected for a film of acid solution 1 molecule thick, strongly suggests that the "saturation" point is connected with the formation of the thinnest possible complete layer of aqueous acid solution. Although much more acid may be present than is necessary to form such a film, it seems highly improbable that one can be formed before the point (R_2, T_2) on the time/resistivity curve is reached. Long before this stage, the material is practically useless as an insulator, so that a natural consequence of this hypothesis is that the time taken for the insulator to become unusable may be dependent, not only on the rate of production of acid by exposure, but also on any surface conditions which affect the formation of conducting paths by combination of isolated portions of acid. The time taken to reach a resistivity of, say, 10^{14} ohms may not be a true measure of the chemical stability of the material. Consequently it is of importance to enquire further into the conditions existing in these early stages. Before doing so it is of interest to calculate some of the quantities of material involved in the formation of the thinnest possible layer. A uniform film of acid solution 2.7×10^{-8} cm. thick and at 75% R.H. would contain $\frac{32}{98} \times \frac{tC_HD_H}{100}$ g. per sq. cm. of sulfur ($= 3 \times 10^{-9}$ g. per sq. cm.) and double that quantity of oxygen, excluding that in the water molecules. These quantities of sulfur and oxygen are contained in layers 8×10^{-9} and 2×10^{-5} cm. thick of hard rubber and air, respectively. As a rough check on the order of magnitude of the quantities involved, a sample which had been exposed for 62.5 standard hours and had reached a resistivity of 10^7 ohms was washed in 10 cc. of distilled water. The p_H value of the water then indicated the presence of about 5×10^{-6} g. of H_2SO_4, while the apparent quantity calculated from the conductivity of the surface was a little over 10^{-7}. The latter value is con-

siderably smaller than the former as would be expected with a non-uniform thickness of acid.

The difference between these two values is partly accounted for by ionic migration, which takes place in the acid film during the interval of 2 minutes between the application of potential and the measurement of resistance. The sulfuric acid-conductivity curve in Fig. 8 was obtained presumably under such conditions that migration of ions could not occur. A decrease in conductivity by a factor 3 or more is probable in this case, resulting in a corresponding underestimate of the quantity of acid present.

Conditions Later than Time T_2.—The course of the later portion of the log T/log R curve, after time T_2, is defined by the constant C. This, in the few cases already noted, is about 0.8–1.0. The average value observed in a number of experiments, some of which are not reported here, is 1 within the limits of experimental error. This implies that the relation between T and R takes the simple form $\frac{1}{R} = \frac{1}{R_2 T_2}$. T or conductivity is proportional to total time of exposure. If the film were of

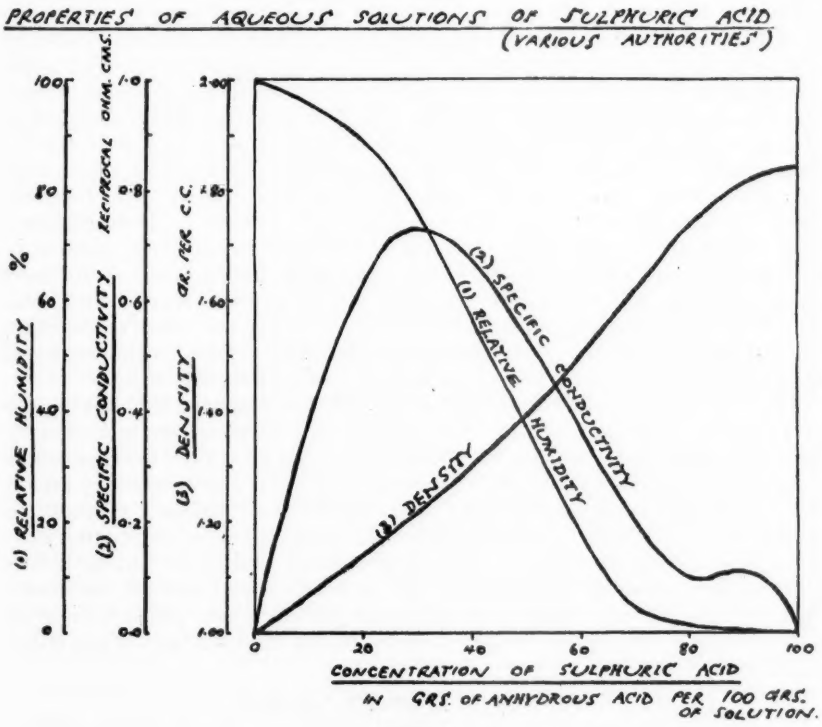
PROPERTIES OF AQUEOUS SOLUTIONS OF SULPHURIC ACID
(VARIOUS AUTHORITIES)
(1) RELATIVE HUMIDITY %
(2) SPECIFIC CONDUCTIVITY RECIPROCAL OHM. CMS.
(3) DENSITY GR. PER C.C.
(2) SPECIFIC CONDUCTIVITY
(1) RELATIVE HUMIDITY
(3) DENSITY
CONCENTRATION OF SULPHURIC ACID
IN GRS. OF ANHYDROUS ACID PER 100 GRS. OF SOLUTION.

Figure 8

uniform thickness, this would mean that the quantity of acid formed was proportional to time of exposure, since the humidity and therefore concentration, density, and specific conductivity were constant. Although the shape of the time-resistivity curve at first sight suggested an autocatalytic reaction, it now appears equally

probable that acid is produced at a constant rate from the beginning of exposure but that it is prevented from manifesting itself in the early stages by its discontinuity.

In this connection it is of interest to see what the form of $T/\log R$ curve would be if the rate of production of acid were the same throughout as it is in the later stages, and if a uniform film could be formed at once. Since the initial conductivity in such a case would be due entirely to volume leakage, a constant volume leakage current must be added to the variable surface current. The calculated $T/\log R$ curve, so obtained, assuming the volume conduction to correspond to a resistivity of 10^{19} ohms, is shown dotted in Fig. 2(*b*). The induction period on this curve is of the order of 10^{-10} hour, hence it is evident that the induction period observed experimentally cannot be explained merely by the fact that initially the greater part of the conduction is due to the constant volume leakage. It follows that either there is a lag in the production of acid, or else this does not at first form a uniform film.

Conditions before Time T_2.—It is difficult to visualize quantitatively the formation of a conducting film, the mathematical theory being complicated, but it appears that a time-resistivity curve of approximately the observed form would be produced by the appearance of separate molecules or groups of molecules of acid, increasing in number and probably size with time of exposure, and coalescing, as the average distance between them decreased, until conducting paths were formed from one electrode to the other. In Fig. 2(*b*) it is seen that the time taken to reach the beginning of the straight "saturation" portion of the curve is about 8 times as great as the time taken for the resistivity to begin falling appreciably. It is supposed that the quantities of acid present are in proportion to the time, and that at the beginning of "saturation" a complete layer is formed. If we consider a chessboard with only 8 pawns on it, it will be seen that the number of possible arrangements in which a complete chain of men stretches from one side of the board to the other, the men being adjacent either forward or diagonally, is very small compared with the arrangements in which there is at least one break in the chain. It is not difficult, therefore, substituting the insulating surface for the board and acid particles for the pawns, to account for the observed induction period.

(The number of complete chains on the 8 by 8 lattice suggested is 11,934 out of a total number of combinations of 4,426,165,368, so that the chance of a complete chain with eight men is about 1 in 370,887. It should be noticed that the chance of obtaining a complete chain with n men on a lattice n by n decreases very rapidly with increase in n, being, for example, 1 in 27, or 2046, or 370,887 for $n = 4$, 6, and 8, respectively. This would mean that to obtain equal chances of conducting paths on the insulator surface, relatively greater amounts of acid are needed as the area of the surface increases. Assuming the rate of production of acid per unit area is constant, this involves a longer time as the test-piece increases, and so a longer induction period. This seems to offer a crucial test of the usefulness of the lattice analogy.—T.R.D.)

Influence of Humidity Changes

Hitherto, the discussion has been confined to the case of material exposed and measured at 75% R.H. Consider next the effects of changes of humidity of measurement. If a deteriorated specimen with a continuous covering of acid were exposed to atmospheres of various humidities the resistivity would be expected to vary in proportion to $C_H D_H / K_H$, x being constant. We should therefore expect the final ("saturation") parts of the log $T/\log R$ curves (2) and (4) in Fig. 3(*b*) to be parallel straight lines distant 0.26 (= log 0.036/0.020) apart on the

logarithmic ohm scale. The curves do not extend far enough for this to be verified quantitatively, but they lie in the right order, and the form of the curves is quite consistent with the above theoretical deduction. The volume of liquid per sq. cm. would vary according to the value of $\frac{1}{C_H D_H}$, x being constant, so that a smaller quantity of acid would be required to form a continuous film at a higher humidity. This is in agreement with the observed decrease of T_2 with increase of humidity of measurement.

The essence of the hypothesis now put forward is that, in the intermediate portion of the exposure, a small increase of liquid on the surface produces a large fall of resistivity primarily because it increases the number of conducting paths, and not because it increases the effective cross section of existing paths. Some light is thrown on this point by the experiments on effects of the humidity of measurement. Consider, for example, sample A at 75% R.H. after 8.5 standard hours' exposure (Figs. 3(*a*) and 3(*b*)). The volume of liquid on the surface may be increased either by further exposure without change of humidity or by increase of humidity without further exposure. An increase of humidity to 97% R.H. would increase the volume of liquid in proportion to $\frac{1}{C_H D_H}$, *i. e.*, from 1 to 4.4. The corresponding observed change of conductivity of the surface was from $1/2.8 \times 10^{15}$ to $1/10^{13}$ ohms (1:280). This change is due not only to changes of volume and distribution of liquid, but also to change of specific conductivity, which must be allowed for in considering the effect of the first two factors. If the specific conductivity of the liquid had remained constant the change in the conductivity of the film would have been $1:680 \left(= 280 \times \frac{0.73}{0.30} \right)$, which is incomparably greater than the proportional change in volume of liquid. This disproportion between the changes in liquid volume and conductivity caused by altering the humidity of measurement shows that factors other than mere volume of liquid are involved, and there is no reason to suppose that the same does not apply when the change in liquid volume is caused by altering the exposure period. Hence it is not necessary to assume a non-uniform rate of acid formation to explain a highly disproportionate rate of change in conductivity.

Actually, the increase in conductivity caused by continued exposure was even more out of proportion to the assumed change in liquid volume than in the case where this change was caused by altering the humidity. Thus, a change in conductivity in the ratio 1:680 was produced by prolonging the exposure by 3.5 hours, and therefore (assuming the rate of acid production to be constant) increasing the liquid volume in the ratio of 1:1.4. As the corresponding ratio in the case where the changes were produced by altering humidity was 1:4.4, it seems that either (*a*) the acid is not produced in proportion to time of exposure, or (*b*) the distribution of acid is affected differently by exposure and by varying humidity. It is difficult to say to what extent either of these factors comes into play, for in connection with (*a*) there is no proof that the rate of formation of acid is either constant or not constant. Incidentally, the shape of the log T/log R curve cannot be explained merely by assuming that the formation of acid is autocatalytic (*i. e.*, most rapid between T_1 and T_2), and that the surface conductivity is proportional to the amount of acid (as would occur, for example, if a uniform film were formed from the start), for if that were the case the value of T_2 should not be affected by varying the humidity of measurement, whereas in reality it is so affected. In regard to (*b*) there is reason to

expect that the effects of humidity and exposure variations would differ in magnitude, although similar in nature, because the former would presumably alter the size of existing acid nuclei while the latter would primarily affect their number. There is some experimental support for this view, because the effects of varying humidity and varying exposure period, as shown by the humidity/log R and T/log R curves, are not quantitatively related in any way which can be explained at present, but the general similarity is shown by the fact that the resistivity is comparatively insensitive to variations in both humidity and exposure during the "induction" and "saturation" periods, and much more sensitive during the intermediate stage of rapid change.

Influence of Loading Ingredients

The case of quality B is more complicated than that of quality A, owing to the presence of a number of unknown ingredients. However, most of the outstanding points of difference in behavior seem to be capable of explanation by the presence in the unexposed material of hygroscopic substances, such as mineral salts, and other substances which can react with the sulfuric acid formed during exposure to light. It has been pointed out previously (*J. Rubber Res.*, **5**, 131 (1936)) that water-soluble substances do not absorb water until the water vapor pressure in the atmosphere reaches that of the saturated solution of the salt concerned. This occurs at a comparatively high relative humidity with many salts. On the other hand, sulfuric acid is hygroscopic over the whole range of humidity. This would explain why, in contrast with quality A, quality B is so sharply affected by humidity above about 85% R.H. So far as can be judged from the present work, the action on exposure to light is probably as follows. Before exposure the quantity of moisture, if any, on the surface at 75% R.H. is so small as to be discontinuous and therefore non-conducting, while at 97–100% R.H. it is sufficient to form a conducting but incomplete film. The primary effect of the appearance of sulfuric acid during exposure is to increase the hygroscopicity over the whole range of humidity. Owing to the presence of some initial moisture on the surface at high humidities, less new liquid is required to form a conducting film than is required for quality A, especially at 97–100% R.H., where an incomplete conducting film exists from zero time, so the induction period is reduced or eliminated. Meanwhile, basic ingredients react with the acid at a limited rate, which is insufficient for neutralization of the acid as fast as it is formed in bright light. If the specimen is removed from light, neutralization continues, giving products which are less hygroscopic and/or less conducting at 75% R.H. than the acid, so that the resistivity of the sample shows recovery (Section III). If the exposure to light is continuous, the fraction of residual free acid increases with the intensity of the light, so that if the exposure is expressed in standard hours the resistivity appears to fall more rapidly in bright than in dull light (Section VI). At 100% R.H., owing to the great hygroscopicity of both acid and salts, a complete film is formed at an early stage, the material being at no time superior to quality A (Section IV).

SUMMARY

Section I. Methods are described for exposing samples of hard rubber to light and measuring their resistivity, both under controlled conditions of humidity.

Section II. The effects of the following experimental conditions were investigated in preliminary tests: surface polish on specimen; type of material—loaded and unloaded; humidity of exposure; humidity of measurement; nature of light—direct sunlight and north daylight; thickness of wall of glass exposure tube; type of glass—ordinary and Vitaglass.

Section III. The variation of surface resistivity at 75% R.H. with time of exposure at 75% R.H. was investigated in the case of a high grade unloaded (A) and a low grade loaded (B) hard rubber.

It was found that there were three well-defined stages in deterioration: (*a*) an "induction period," during which the resistivity remained practically unchanged; (*b*) a period during which the resistivity fell very rapidly, and (*c*) a "saturation period," during which the resistivity, having reached a low value of about 10^7–10^8 ohms, continued to fall relatively slowly. The log time/log resistivity curve was found to be reducible to a simple mathematical form, in accord with which all the results in the report are analyzed. Quality A, although initially superior to B, deteriorated more rapidly and to a greater extent. The resistivity of B increased slowly on removal from the light.

Section IV. The surface resistivity of quality A was sensitive to the humidity during measurement, except with samples in the "induction" and "saturation" stages; that of quality B was more sensitive to humidity at all stages between 85 and 100% R.H., but less so at lower humidities. At 97 and 100% R.H., B was in all respects inferior to A, its apparently greater stability at 75% R.H. being due to its lower hygroscopicity at normal atmospheric humidities.

Section V. When the humidity of exposure was varied there was a maximum rate of deterioration at 70–90% R.H. in the case of quality A, both dry and saturated conditions having a retarding effect.

Section VI. In artificial light (at 15 cm. from a 100-watt gas-filled lamp) the deterioration was slower than in bright north daylight, but for quality A the rate was the same in both cases if expressed in terms of standard hours as measured by a photographic exposure meter. Quality B deteriorated relatively less rapidly in the artificial light, a phenomenon probably connected with that of recovery of resistivity; and it is pointed out that accelerated or artificial light aging tests cannot yet be accepted as giving a true measurement of relative stability in sunlight.

Section VII. The mechanism of formation of a conducting film is discussed. It is considered that (*a*) a complete layer of acid cannot be formed before the beginning of the "saturation" period; (*b*) the assumption that acid formation is due to an autocatalytic reaction is neither necessary nor sufficient to explain the results obtained; (*c*) the first and second stages of deterioration correspond to a period in which acid nuclei are formed, and increase in number and/or size to form conducting paths; (*d*) the changes of resistivity with humidity are explainable in a similar way; and (*e*) the difference in behavior between qualities A and B are due to the presence in B of water-soluble and/or acid-soluble substances which take part at a limited rate in secondary reactions with the acid as it is formed.

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Studies on Vibration Tests of Rubber

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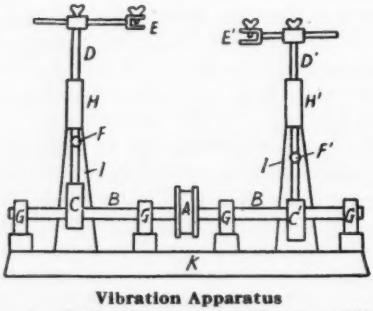
Introduction

It is well known that certain metals crack or become less flexible when subjected to vibration. For instance, suspending wires of lead, lead-zinc alloys, etc., in air increases their brittleness until finally they can be broken, even by bending slightly.

The present paper deals with experiments the object of which was to ascertain the effect of keeping rubber in a state of vibration. It was thought that the results might have some influence in practical problems.

Apparatus and Technic

The vibration apparatus was constructed as shown in the sketch. The samples were vulcanized sheets 20 cm. long, 10 cm. wide, and 1.5 mm. thick. The sample is supported at E, E′, and A is driven by a 0.25 H. P. motor at 1425 revolutions per minute. C, C′ are connected to the main axis in such a way that the distance from the center of the main axis is 6 mm. and the rods D, D′ attached to C, C′ move up and down 6 mm. through the guide H, H′. The sample is thus vibrated 1425 times per minute with an amplitude of 12 mm.



Vibration Apparatus

A. Pulley Connected to Motor; 1425 Revolutions per Minute
B. Main Axis
C, C′. Eccentric Top, Moving Distance 6 mm.
H, H′. Guide for Vertical Motion
E, E′. Sample Holder
G. Bearings
K. Base
The Angle of Eccentrics, C, C′, Can Be Changed from 90° to 180°

Experimental Results

The object of the work was to ascertain what changes, other than visible ones, occur as a result of vibration. The following points were studied individually.

1. What is the direct effect of vibration?
2. What is the effect of the time of vibration?
3. What is the effect of the percentage of rubber and of the degree of vulcanization?

Various experiments were made to answer these questions, but the experiments were not carried far enough to draw general conclusions, and it is necessary to continue them. The results obtained so far are as follows.

Vibration for 50 Hours

Thirteen samples were vibrated for 50 hours (total vibrations 4,275,000) in a

laboratory at 30° C. After vibration they were kept in a desiccator for 10 hours and their electrical and mechanical properties determined.

Size and Hardness.—At the center of each sample a mark (5 cm. × 10 cm.) was printed before the vibration test, and the change in dimensions of this mark was accurately measured after vibration. The results indicated that with normally or overvulcanized rubber there were no changes in size or hardness.

Electrical Properties.—The most definite result of the vibration experiments was the discovery of changes in electrical properties, the most noteworthy change being a lowering of insulation resistance. The results of the 50-hour vibration tests are shown in Table I.

TABLE I

ELECTRICAL PROPERTIES

Sample	Elec. Properties	Untreated (N)	50 Hours' Vibration (V)	$V/N \times 100$
A	Dielec. const.	61.48	31.67	51.5
	Insulating resis.	1.180×10^5	5.738×10^4	48.6
	Puncture voltage	7,480	8,070	107.8
B	Dielec. const.	60.72	37.93	62.4
	Insulating resis.	3.020×10^5	9.490×10^4	31.4
	Puncture voltage	9,460	11,060	116.9
C	Dielec. const.	6.675	7.793	116.7
	Insulating resis.	1.472×10^8	1.040×10^7	7.0
	Puncture voltage	20,690	19,830	95.8
D	Dielec. const.	9.363	9.790	104.5
	Insulating resis.	1.069×10^8	9.200×10^7	86.0
	Puncture voltage	18,590	18,150	97.0
E	Dielec. const.	23.89	37.01	154.9
	Insulating resis.	4.948×10^6	2.248×10^6	49.1
	Puncture voltage	12,200	10,760	88.1
F	Dielec. const.	2.887	3.376	117.3
	Insulating resis.	3.540×10^8	1.857×10^8	52.45
	Puncture voltage	26,110	23,680	90.7
G	Dielec. const.	5.250	5.602	106.7
	Insulating resis.	1.326×10^7	1.326×10^6	10.0
	Puncture voltage	13,270	12,820	96.6
H	Dielec. const.	4.826	5.410	112.1
	Insulating resis.	1.229×10^8	6.638×10^6	5.4
	Puncture voltage	21,770	19,920	86.9
I	Dielec. const.	3,478	9,735	279.8
	Insulating resis.	99.6	71.6	71.9
	Puncture voltage	1,700	1,610	94.7
J	Dielec. const.	7,037	8,935	127.0
	Insulating resis.	57.1	45.7	80.0
	Puncture voltage	1,520	1,340	81.5
K	Dielec. const.	1,126	2,285	202.9
	Insulating resis.	3.027×10^2	2.175×10^2	70.1
	Puncture voltage	2,060	1,760	85.4
L	Dielec. const.	10,460	9,483	90.6
	Insulating resis.	1.490×10^7	1.628×10^7	109.2
	Puncture voltage	15,730	16,830	107.0
M	Dielec. const.	6.085	3.943	64.8
	Insulating resis.	3.910×10^7	7.518×10^6	19.2
	Puncture voltage	25,108	24,090	95.9

Samples A, B, C, D, E, and F contained 60 per cent rubber; G, 70 per cent rubber; H, 55 per cent rubber; I, 35 per cent rubber, all vulcanized at 145° for 30 min.; J, 35 per cent rubber, vulcanized at 145° for 120 min.; K, 35 per cent rubber, vulcanized at

Table II

Result of Water Absorption Test

Soaking (Hours)	Sample A				Sample B				Sample C			
	Cold Water		Boiling Water		Cold Water		Boiling Water		Cold Water		Boiling Water	
	Control	Vibrated	Control	Vibrated	Control	Vibrated	Control	Vibrated	Control	Vibrated	Control	Vibrated
1	0.003	0.040	0.031	0.460	0.010	0.020	0.280	0.350	0.006	0.010	0.470	0.500
	100	100	100	100	100	100	100	100	100	100	100	100
2	0.008	0.070	0.490	0.650	0.030	0.040	0.390	0.470	0.010	0.020	0.580	0.740
	266	175	158	141	300	200	139	134	167	200	123	148
3	0.020	0.080	0.590	0.830	0.050	0.050	0.480	0.580	0.010	0.040	0.860	0.930
	666	200	190	180	500	250	171	166	167	400	183	186
5	0.070	0.120	0.900	1.160	0.060	0.070	0.670	0.770	0.020	0.050	1.150	1.220
	2333	300	290	252	600	350	239	220	333	500	245	244
10	0.080	0.190	1.550	1.850	0.110	0.170	1.130	1.310	0.160	0.210	1.860	2.030
	2666	475	500	462	1100	850	404	274	2667	2100	398	406
15	0.110	0.220	1.950	2.310	0.150	0.200	1.480	1.750	0.180	0.220	2.470	2.770
	3667	550	629	502	1500	1000	529	500	3000	2200	526	554
$V/C \times 100$		200		118		133		118		122		112
	Sample D				Sample E				Sample F			
1	0.007	0.009	0.370	0.390	0.003	0.006	0.370	0.400	0.070	0.130	0.760	0.960
	100	100	100	100	100	100	100	100	100	100	100	100
2	0.010	0.030	0.570	0.600	0.010	0.010	0.550	0.590	0.100	0.180	1.480	1.740
	142	233	154	154	333	167	149	145	143	138	195	181
3	0.020	0.050	0.680	0.770	0.020	0.020	0.710	0.780	0.140	0.190	2.090	2.470
	286	556	184	197	666	333	192	195	200	140	275	257
5	0.040	0.070	0.920	1.000	0.040	0.070	1.010	1.030	0.210	0.300	3.080	3.620
	571	778	249	256	1333	1166	273	257	300	231	405	377
10	0.080	0.130	1.400	1.510	0.100	0.120	1.670	1.760	0.270	0.360	5.410	5.900
	1043	1444	378	387	3333	2000	451	440	386	276	712	601
15	0.110	0.170	1.870	2.000	0.175	0.210	2.230	2.410	0.330	0.410	7.160	7.540
	1571	1889	505	514	5833	3500	602	603	471	315	942	709
$V/C \times 100$		155		107		120		108		124		105

	Sample G				Sample J			
1	0.200	0.490	5.470	5.490	0.002	0.005	0.120	0.130
	100	100	100	100	100	100	100	100
2	0.200	0.600	8.540	8.680	0.004	0.005	0.180	0.180
	150	122	156	158	200	100	150	138
3	0.390	0.720	10.83	10.84	0.005	0.010	0.220	0.220
	195	147	198	198	250	200	183	175
5	0.590	1.170	16.35	16.94	0.008	0.020	0.280	0.310
	295	239	299	308	400	400	233	238
10	1.260	1.960	32.93	33.11	0.030	0.040	0.410	0.450
	630	400	602	603	1500	800	342	346
15	1.740	2.670	51.67	52.40	0.045	0.600	0.470	0.510
	870	549	944	954	2250	1200	391	392
$V/C \times 100$		153		101		133		109
	Sample I				Sample L			
1	0.002	0.002	0.130	0.130	0.005	0.008	0.740	1.010
	100	100	100	100	100	100	100	100
2	0.002	0.005	0.200	0.210	0.030	0.040	1.020	1.340
	100	250	154	162	600	500	138	133
3	0.005	0.009	0.230	0.250	0.060	0.080	1.310	1.720
	250	450	177	192	1200	1000	177	170
5	0.010	0.030	0.310	0.330	0.100	0.160	1.740	2.320
	500	1500	2348	254	2000	2000	235	220
10	0.050	0.060	0.460	0.520	0.250	0.340	2.640	3.650
	2500	3000	354	192	5000	4250	357	361
15	0.650	0.075	0.630	0.670	0.310	0.470	3.560	4.890
	3250	3750	485	515	6200	5875	481	484
$V/C \times 100$		115		108		152		137

The upper line is in each case the per cent water absorption, the lower line is the water absorption calculated on the basis of 1-hour soaking = 100.

V is the water absorption of vibrated samples after 15 hours' soaking. C is the water absorption of the control after 15 hours' soaking.

The average water absorption of the various samples after 15 hours' soaking in cold water was 0.322 per cent; after 50 hours' vibration and 15 hours' soaking in cold water it was 0.471 per cent.

The average water absorption of the various control samples after 15 hours' soaking in boiling water was 7.349 per cent; average water absorption of the various samples after 50 hours' vibration and 15 hours' soaking in boiling water was 7.725 per cent.

145° for 180 min.; L, 75 per cent rubber, vulcanized at 130° for 20 min.; M, 90 per cent rubber, vulcanized at 145° for 30 min. The insulating resistance is expressed as megohms per cc.; the unit of puncture voltage was *v/mm.*

The dielectric constant was measured by a movable circular ammeter (sensitivity 10^{-10} amp.) with a d. c. of 50 v.; the temperature was kept at 30° C., the relative humidity at 70–85 per cent.

The insulating resistance was measured with a d. c. of 600 v. The puncture voltage was measured with a circular electrode 12.5 mm. in diameter.

Samples A to F contained 60 per cent rubber, but different compounding ingredients. It was found that in general as the dielectric constant increased, the puncture voltage decreased, and the insulating resistance decreased greatly.

Samples I to K contained 35 per cent rubber and the same compounding ingredients, but the degrees of vulcanization differed. Samples of low rubber content gave lower puncture voltages and insulating resistances. Samples L and M, containing larger percentages of rubber, gave lower dielectric constants and slightly higher puncture voltages. The insulating resistance diminished in the same way as in preceding cases.

Ordinarily, rubber to be used for electrical insulation should have a low dielectric constant, high insulating resistance, and high puncture voltage.

Water Absorption.—Vibration changed noticeably the water absorption. In boiling water the absorption was far greater than at room temperature.

Samples after vibration were cut into circular discs 44.6 mm. in diameter and immersed in water for various times. After removal the adhering water was wiped off with a soft cloth, and the samples were weighed quickly. The results are shown in Table II. The water absorption before and after vibration was calculated in percentages for comparison. The rates of increase of water absorption in boiling water were not great in percentages, but the actual amounts of water absorbed reached 2 or 3 times as much as the amounts after immersion in cold water.

Mechanical Properties

Samples before and after vibration were cut into rings having an inner diameter of 44.6 mm. and an outer diameter of 52.6 mm., and their tensile strengths and elongations were measured on an improved Scott apparatus. The temperature of the laboratory was at 30° C., and the test-pieces were kept at this temperature for 24 hours before testing.

To measure permanent elongation, a mark 5.0 mm. long was printed on the central part of the test-piece, which was 5 mm. wide and 100 mm. long; this was stretched 3 times its original length, was held for 1 minute, was released, and the percentage permanent elongation was measured after 10 minutes. The results are shown in Tables III and IV.

It is clear from these tables that the tensile strength and elongation were slightly diminished by the vibration, while the permanent elongation increased slightly.

The Effect of Changing the Time of Vibration

As it was found in the preceding experiment that vibration for 50 hours changed slightly the properties of rubber, further experiments were carried out to ascertain the effect of changing the time of vibration on these changes in properties.

Electrical Properties of Rubbers Measured by the Difference in Time of Vibration.—A comparison of a continuous 100-hour period of vibration with a 50-hour period of vibration (Table I, Sample H) for the same sample gave the following results:

Table III

Tensile Strength and Elongation before and after Vibration

Sample	Tensile Strength		Elongation			
	Control (*N*)	Vibration for 50 Hours (*V*)	Control (*E. N.*)	Vibration for 50 Hours (*E. V.*)	$V/N \times 100$	$E.\ V./E.\ N. \times 100$
A	1.020	0.910	301.7	273.7	90.3	90.7
B	0.960	0.886	338.0	319.0	92.3	94.3
C	1.155	1.170	528.8	516.3	101.3	97.6
D	1.092	1.032	442.5	434.8	94.5	98.2
E	0.964	0.898	378.5	361.3	93.1	95.4
F	1.400	1.358	588.0	619.0	96.9	105.3
G	0.052	0.061	71.3	84.0	118.4	117.8
H	2.000	1.923	967.5	688.0	96.2	98.6
I	1.352	1.314	245.5	238.0	97.1	96.9
J	1.150	1.096	211.0	202.0	95.3	95.7
K	1.026	1.008	207.0	200.0	98.0	96.8
L	1.032	1.075	408.2	406.0	104.1	99.5

Tensile strength is expressed in kg. per sq. mm.; elongation in per cent.

Table IV

Permanent Elongation before and after Vibration (After Stretching 3 Times)

Sample	Control	Vibration for 50 Hours
A	7.33	10.5
B	5.4	5.0
C	2.23	2.47
D	2.75	2.57
E	4.67	5.15
F	3.25	3.13
G	0.5*	0.3*
H	4.0	4.5
I	14.1 ×	14.35×
J	13.6 ×	13.83×
K	13.73×	13.60×
L	11.9	11.0

* Elongated 50 per cent of original length × elongated 200 per cent.

Table V

Treatment	Dielec. Const.	Insulation Resistance (Megohm per Cc.[3])	Puncture Voltage (V. per Mm.)
Control (*C*)	4.826	1.129×10^8	21,770
50 Hours' vibration (*D*)	5.410	6.638×10^6	19,920
100 Hours' vibration (*E*)	7.325	5.437×10^6	18,080
$D/C \times 100$	112.1	5.4	86.9
$E/C \times 100$	151.7	4.4	82.5

Table VI

Treatment	Dielec. Const.	Insulation Resistance (Megohm per Cc.[3])	Puncture Voltage (V. per Mm.)
Control (*C*)	4.530	1.790×10^8	24,590
5 Hours' vibration (*P*)	4.820	1.543×10^8	25,100
10 Hours' vibration (*Q*)	4.670	1.433×10^8	24,080
15 Hours' vibration (*R*)	5.290	1.277×10^8	23,830
20 Hours' vibration (*S*)	5.095	1.311×10^8	21,480
$P/C \times 100$	106.4	86.3	102.0
$Q/C \times 100$	103.0	80.1	97.9
$R/C \times 100$	116.8	71.4	96.9
$S/C \times 100$	112.4	73.3	87.3

The tests on the new sample containing 60 per cent rubber after 5, 10, 15, and 20 hours' vibration are shown in Table VI.

The preceding two experiments show that the dielectric constant increases and the puncture voltage and insulating resistance diminish even after vibration for a very short time, and that these changes continue for long periods at a comparatively slow rate as long as vibration is continued.

The samples in Table VI were also tested for their resistance to surface leakage and their sparking voltage.

TABLE VII

Treatment	Resistance to Surface Leak (Megohm per Cc.[2])	Sparking Voltage (V. per 2 Cm.)
Control	4.984×10^5	17,000
5 Hours' vibration	5.043×10^5	17,000
10 Hours' vibration	4.803×10^5	17,000
15 Hours' vibration	4.763×10^5	16,900
20 Hours' vibration	4.976×10^5	16,900

The object of these experiments was to ascertain any deterioration of the surface. The results show that there was a slight deterioration with time of vibration.

Mechanical Properties of Rubber as Affected by the Difference in Time of Vibration.—The results of electrical tests after 5, 10, 15, and 20 hours' vibration of the sample containing 60 per cent rubber are given in Table VI. The mechanical properties of these samples are given in Table VIII.

TABLE VIII

Treatment	Tensile Strength (Kg. per Sq. Mm.)	Elongation (Percentage)
Control	0.749	645
5 Hours' vibration	0.873	663
10 Hours' vibration	0.976	667
15 Hours' vibration	1.064	673
20 Hours' vibration	1.039	670

TABLE IX

Sample	Decrease in Thickness (Percentage)	Insulating Resistance (V. per Mm.) Before Stretching	Insulating Resistance (V. per Mm.) After Stretching	Tensile Strength (Kg. per Sq. Cm.) Before Stretching	Tensile Strength (Kg. per Sq. Cm.) After Stretching	Elongation (Percentage) Before Stretching	Elongation (Percentage) After Stretching
A	27.0	7,790 (100%)	12,410 (159.3%)	1.020	1.002	301.7	321.7
B	35.7	9,910 (100%)	17,070 (172.2%)	0.960	0.998	338.0	359.0
C	32.6	1,1780 (100%)	18,040 (153.0%)	1.155	0.930	528.8	394.0
D	36.2	1,3720 (100%)	21,580 (157.3%)	1.092	0.855	442.5	441.7
E	25.0	2,1050 (100%)	27,880 (132.4%)	0.964	1.002	378.5	507.7

These data show that the tensile strength and elongation at break increase to a certain extent with an increase with the time of vibration.

Effect of Stretching.—The effect of vibrating rubber is described in the foregoing experiments. Since the changes may have been caused by the creation of some internal strain, the changes in properties after stretching were studied.

The sample used in the preceding experiments was stretched to twice its original length by another stretching apparatus and was kept stretched for 2 hours; the electrical properties were then measured while the rubber was stretched, and the mechanical properties were measured immediately after releasing.

The electrical properties, especially the puncture voltage, showed a remarkable increase, but an accurate comparison is not possible because the thickness was decreased by the stretching. There was no remarkable change in mechanical properties. The results are given in Table IX.

Summary

Experiments were carried out to determine the resistance of rubber products to vibration. There were no essential changes in mechanical properties as a result of vibration for 50 to 100 hours. There were on the other hand considerable changes in electrical properties, *e. g.*, the insulation resistance decreased with increase in time of vibration.

Further experiments in connection with this problem will be carried out to obtain data on the effects of vibration for prolonged periods.

The authors wish to thank Messrs. Endo, Taguma, Hamono, and Wada for their aid in the experimentation.

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Rubber-Lined Equipment

Fundamental Principles of Design

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THE B. F. GOODRICH COMPANY, AKRON, OHIO

IN 1924 a process known as Vulca-lock, discovered by chemists of The B. F. Goodrich Company, made possible the first successful steel tank car for hydrochloric acid service. The tank was lined with acid-resisting vulcanized rubber bonded to the steel shell with adhesion exceeding 500 pounds per square inch. A new material of chemical construction was thus made available in practical form.

The resulting widespread and rapidly increasing use of rubber-lined equipment in the processing industries is well known. Basically, the value of such construction lies in properly combining the unique corrosion- and abrasion-resistant properties of rubber with the rigidity, strength, and adaptability of steel or other structural materials. It is essential, therefore, that chemical engineers be familiar with certain principles of design, upon which the successful use of rubber-lined equipment depends.

No attempt will be made in this paper to define the broad field of usefulness or the limitations of rubber linings. The fact must be emphasized, however, that an extremely wide range of chemical and physical properties is available in commercial rubber compounds and that these compounds, like metals and alloys, are designed for specific uses.

In considering the application of rubber to any chemical project, unless previous experience clearly points the way, the engineer would do well to obtain the coöperation of reliable rubber manufacturers who maintain research facilities and who are constantly studying and improving the usefulness of rubber compounds for specific conditions of service. Too much emphasis cannot be laid upon the necessity for accurate, complete definition of service conditions and requirements. Only through coöperation between the engineers using rubber and the engineers designing it can the best advantage be taken of this unique and versatile engineering material.

While unvulcanized fine Para and pale crepe rubbers have been, and to a very limited extent are still, used as corrosion-resistant linings, the great bulk of rubber applied to chemical service is vulcanized. The present discussion will be limited, therefore, to equipment lined with vulcanized rubber.

FIGURE 1 (*Left*). STEEL TANKS LINED WITH RUBBER AND SHEATHED WITH ACID-PROOF BRICK FOR BILLET PICKLING SERVICE IN A STEEL MILL

A steel rinse tank (unlined) is in foreground. The method of mounting makes all exterior surfaces readily accessible and allows free circulation of air.

FIGURE 2 (*Lower Left*). ROLLING A RUBBER LINING TO ENSURE FIRM CONTACT WITH THE ADHESIVE FILM IN A STEEL TANK

Function of Lining

It is fundamental to bear in mind that the function of rubber linings in chemical equipment is protective, not structural. Such linings are useful only to the extent that they (1) protect equipment from corrosion or abrasion and (2) protect contents from contamination. Structural requirements, such as resistance to pressure or vacuum, must, therefore, be taken care of wholly in the design of the vessel or other part to be lined.

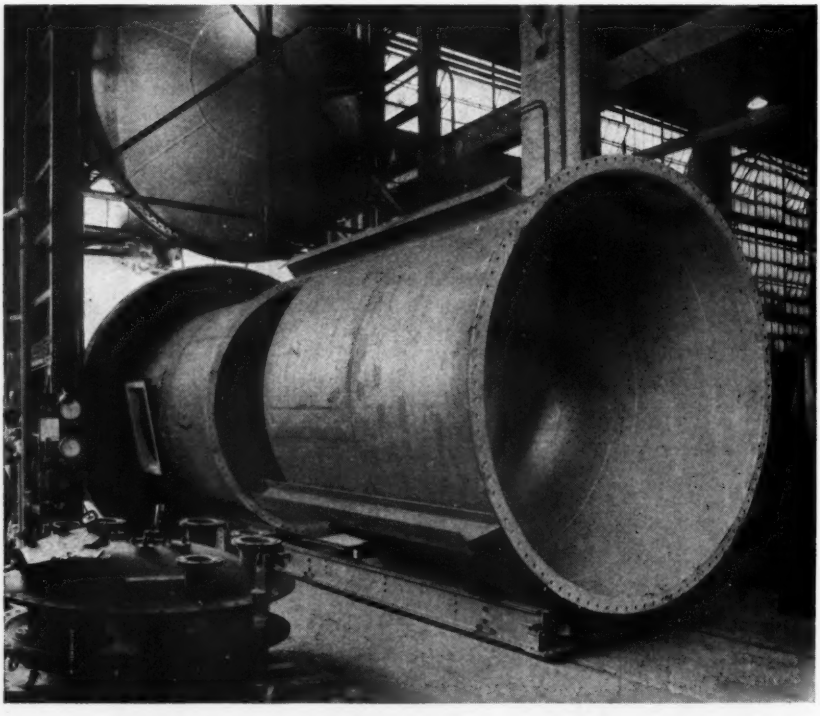


FIGURE 3 TWO-SECTION RUBBER-LINED STEEL TANK ENTERING A LARGE STEAM VULCANIZER

The flanged construction of the tank halves is designed for field assembly. The vulcanizer is 15 feet in diameter and approximately 50 feet long; it is thought to be the largest in the world.

Choice of Materials

Rubber linings can be applied to many different structural materials. There are few cases, however, in which steel is not the logical choice because of low cost, ease of fabrication, strength and rigidity, adaptability to a wide variety of structural and process requirements, adaptability to requirements for successful application of rubber lining, and ease with which alterations and repairs can be made.

For corrosive service, iron and steel vessels possess the fur-

ther advantage that, in case of accidental rupture of the rubber lining, leakage will show up quickly through the shell and (provided proper bonding of rubber to metal has been obtained) directly behind the point of damage to the rubber. Detection can thus be made before the damage becomes extensive. Repairs are made quickly and easily.

Rubber-lined metal tanks should be located so that all exterior surfaces are readily accessible for inspection, painting, and repairs (Figure 1).

In cases where rubber is required to be bonded to alloys, the rubber manufacturer should be consulted for recommendations. There are some limitations in this field. Alloys of high copper, lead, manganese, or silica content are generally to be avoided.

Wood or concrete tanks and other equipment can be satisfactorily rubber lined where structural and process requirements indicate the advisability of such construction.

Application of Lining

A brief description of how rubber linings are generally applied will facilitate an understanding of certain principles which must be followed in designing the equipment. Essential steps in the case of steel are as follows:

(1) Preparation of the metal surface. Areas to be rubber-covered are cleaned and roughened, usually by sand or steel grit blasting.

(2) Application of special adhesives. Generally such materials are spread over the freshly blasted surface in liquid form, like paint. A number of coats are used, often of varying composition. Each coat must be thoroughly dry before the next is applied.

(3) Application by hand of unvulcanized rubber compound in sheet form. The rubber is sticky and semi-plastic at this stage, permitting adjacent sheets to be made integral at the seams. Thorough hand-rolling ensures firm contact with the adhesive film over the entire area (Figure 2). The rubber sheets which are commonly $^3/_{16}$ to $^3/_8$ inch thick, depending upon service requirements, are built up of a large number of very thin layers, plied in a calender.

(4) Vulcanization of the rubber. Best and most uniform results are obtained when steam (or a combination of air and steam) under pressure can be used. This is accomplished by either of the following two methods:

(*a*) Placing the entire rubber-lined part inside a large autoclave (Figure 3).

(*b*) In the case of closed rubber-lined vessels, internal steam under pressure may be introduced, up to the safe limit. Steam pressures of 30 to 75 pounds per square inch are generally employed, with the period of exposure varying from 2 to 8 hours. Where neither of the above methods is applicable, such as in the case of large, open tanks lined in the field, a satisfactory cure can be obtained by more prolonged exposure to boiling water or exhaust steam. Temperature control in this method is likely to be less uniform and accurate than when steam pressure can be used.

In order to obtain the advantages of pressure cure it is often advisable to fabricate extremely large tanks in flanged sections so that they may be accommodated in vulcanizing equipment available at the rubber manufacturer's plant. Such flanged sections are assembled in the field by bolting together with suitable gaskets.

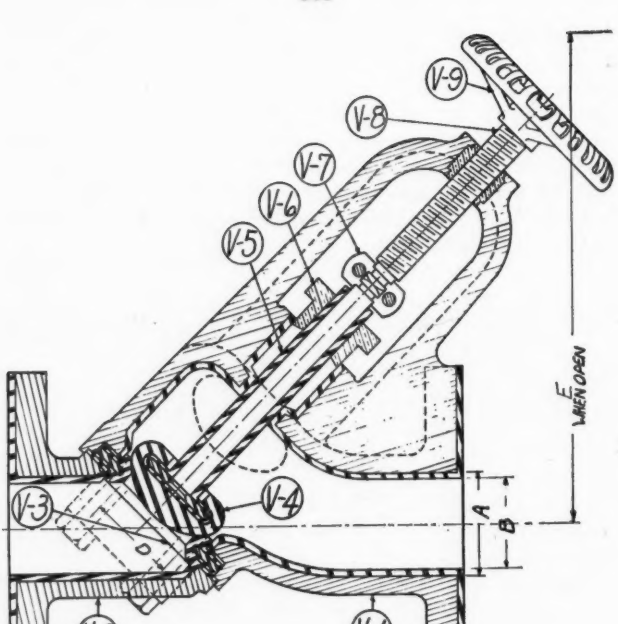


FIGURE 4. STANDARD DESIGN OF RUBBER-LINED VALVE SUITABLE FOR BOTH PRESSURE AND VACUUM SERVICE

The dimensions, in inches, are as follows:

Nominal Size *A*	Size Opening *B*	Length Face to Face *C*	Opening at Seat *D*	Clearance Height *E*
1½	1¼	7¼	1⅜	7⁹/₁₆
2	1⅜	8¼	1⅜	10⁵/₁₆
3	2⅜	10¼	2⅜	14¼
4	3⅜	14¼	3⅜	17⅞
6	5⅜	20¼	5⅜	22⅝

Labor obviously constitutes a very large proportion of the total cost of rubber linings applied to industrial equipment. In many cases, therefore, not only a higher factor of safety but also better value can be obtained by specifying more than the standard $^3/_{16}$-inch thickness of lining in large permanent installations. This is especially true where severe service conditions are anticipated.

Accessibility Fundamental

From the foregoing it is obvious that one of the basic design principles for equipment to be rubber lined is that all surfaces to be covered with rubber must be readily accessible for handwork. There is only one important exception to this rule, and that is in the case of round pipes, where the lining procedure used is somewhat different. In pipe lining, a flattened tube of unvulcanized rubber is drawn through the pipe, which has been previously blasted and cemented. The

rubber tube is then brought into firm, uniform contact with the adhesive film on the pipe walls by applying air pressure inside.

Design of Tanks

With the exception of railroad tank cars, practically all rubber-lined metal tanks today are of welded steel plate construction. Modern welding technic has made this method of fabrication by far the most economical and adaptable. Welded construction, owing to the comparative smoothness and uniformity of the surfaces, is particularly suited to the process of lining and should, therefore, be given first consideration in designing rubber-lined equipment.

The following precautions are necessary on the part of the fabricator:

(1) Joints over which rubber is to be applied must be solid welded.

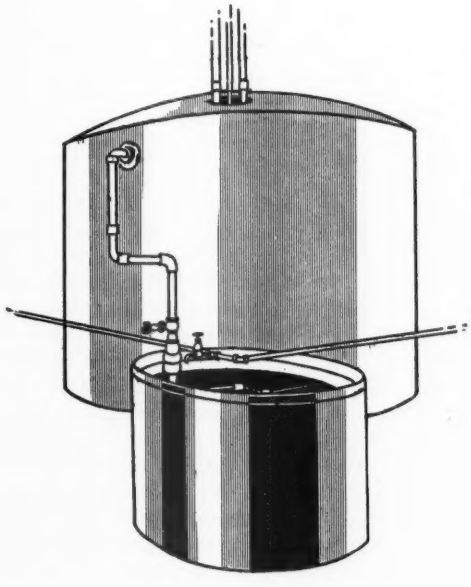
(2) Porosity in the finished welds is not permissible. Porous welds may be peened. Pits, sharp depressions, or porosity are likely to trap air or solvent from the adhesive, causing blisters to form under the lining during cure.

(3) Burrs, excessive weld spatter, and sharp edges must be removed by grinding. Many fabricators have developed their welding technic to the point where a very dense smooth bead is laid on, requiring almost no peening or grinding.

(4) All sharp edges of sheared plates must be removed.

(5) Corners should be rounded to approximately 1/8-inch minimum radius.

(6) Nipple outlets should be made flush with plate inside and corners rounded. Flanges on nipples must be screwed or welded flush with end of pipe (no exposed threads), and corners must be rounded. When screwed flanges are used, they must be peened in place to prevent loosening in service.



Tanks should be closely inspected for finish at the place of fabrication and all defects corrected before shipment is made to the rubber manufacturer. Rubber manufacturers will gladly accept the responsibility of furnishing complete equipment, metal and rubber, and in such cases usually arrange

for their own inspectors to approve each metal part at fabricator's plant before acceptance.

Likewise, tanks for pressure or vacuum service should be tested before lining with rubber and should be made perfectly tight under the specified test conditions. An air leak in the steel tank will cause failure of the rubber lining if the vessel is used under vacuum.

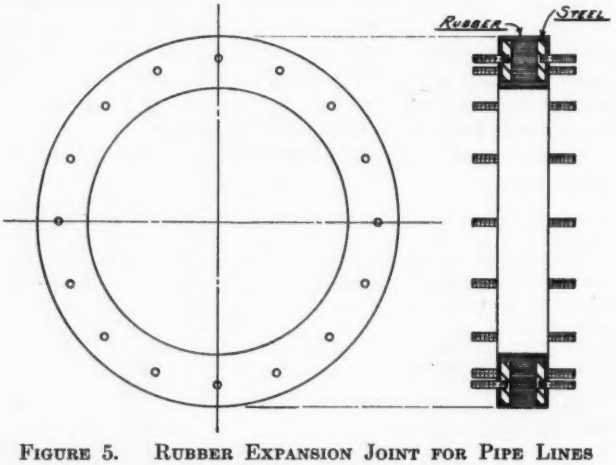


FIGURE 5. RUBBER EXPANSION JOINT FOR PIPE LINES
Practically integral bonding of the soft rubber slab to the steel rings is required for success of this joint.

Sectional tanks for field assembly should be provided with joining flanges of ample size, drilled for bolts (Figure 3). The rubber lining is brought over the faces of these flanges, and suitable soft rubber gaskets are provided to make a tight seal when the flanges are bolted together. In large installations it is advisable further to specify that a rubber sealing strip about 8 inches wide be applied over each joint after assembly. This is simply an added factor of safety.

All outlets in tanks should be of flanged type, with the rubber carried out over the flange faces. This construction readily permits connection to pipes, valves, and other fittings without danger of leakage or contact with metal. Minimum size nipple for best results is $1^1/_2$ inches. The reduction in internal diameter owing to rubber lining should be borne in mind.

If the workmen applying the rubber lining must enter the tank through a manhole, this should be not less than 18 inches in diameter in the interests of safety.

Physical and Thermal Protection

Owing to the natural limitations of rubber in respect to service where mechanical abuse or high temperatures are encountered, protective sheathings are frequently installed within rubber-lined tanks. Tongued and grooved wood lin-

ings often provide the required mechanical protection in such cases, but offer little or no thermal advantage. The best practical method of avoiding the adverse effects of high temperatures is to install a sheathing of suitable acid-proof brick inside the rubber lining. The maximum reduction in rubber temperature is obtained only when a steel tank is used, with reasonably free circulation of air past all exterior surfaces (Figure 1).

This construction is successfully and widely used in the metal industries where pickling operations are normally conducted at temperatures exceeding 175° F. and where, owing to the nature of material handled, mechanical abuse is unavoidable.

Castings

A safe rule to follow in designing equipment to be rubber lined is to avoid the use of large or complex castings whenever possible. Small simple castings, such as standard fittings and flanges, offer no difficulties, provided the following precautions are closely adhered to:

(1) Iron castings must be of close-grain gray iron. (Steel scrap in the mix is permissible for strength.)
(2) Surface to be rubber-covered must be free from excessive porosity. Blow holes or sand holes on the surface may be cleaned out and edges rounded to $1/8$-inch radius or greater. Occasional small porous spots exposed on the surface may be drilled, tapped, and plugged (with steel or iron only) in such a manner that the plug does not trap air or leave exposed cracks, and cannot work loose. The use of lead, babbitt, "smooth on," brazing, or other iron fillers or cements is not permissible.
(3) All corners to be rounded to at least $1/8$-inch radius.
(4) Surface must be free from all sharp projections and fins.

Inasmuch as undesirable porosity often does not become apparent until after blasting, it is well to specify in the case of large castings that the fabricator shall, at the time of inspection, sandblast areas to receive the rubber covering. This will not eliminate the necessity for further blasting at the rubber manufacturer's plant just prior to lining.

Pipe, Fittings, and Valves

Flanged construction is best suited to the majority of rubber-lined pipe installations. Each job is necessarily "tailor-made," since pipe lengths cannot be altered conveniently after lining. Engineers not thoroughly familiar with this type of equipment should pursue either of the two following courses: (1) Draw up details of proposed pipe lines and connections, showing all center-to-face dimensions, and submit such drawings to the rubber manufacturer who will gladly prepare a bill of materials. (2) Consult the rubber manufacturer who will recommend type and thickness of lining to be used and will also advise proper allowance to be made for rubber at joints. The user will then be in a position to list his own bill of materials.

Fittings are commonly of standard cast-iron flanged construction, carefully selected from manufacturer's stock to be sure they are suitable for rubber lining.

Pipe is usually standard wrought steel, with cast-iron flanges screwed on and peened in place. Care must be taken that flanges are made flush with the pipe ends. If steel flanges are required, they may be either screwed on and peened, or welded in place. Bolt holes must be lined up so that pipe will fit properly into the final assembly.

It is advisable in most cases to permit the rubber manufacturer to furnish pipe and fittings complete in order that

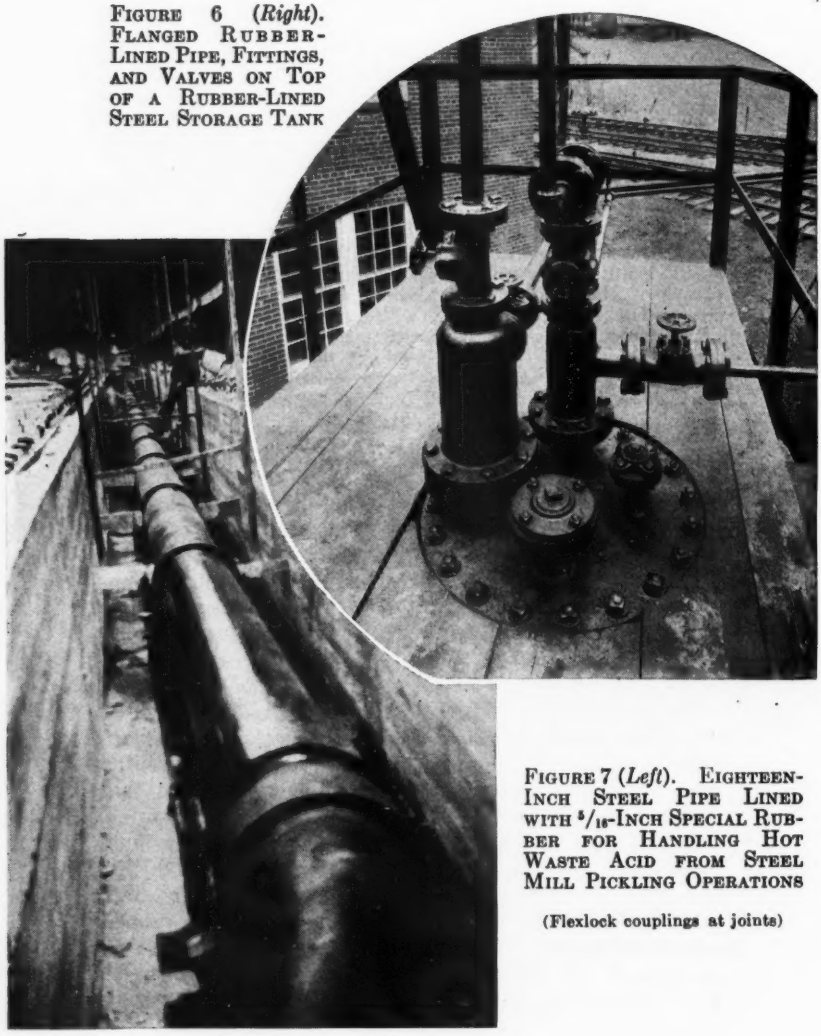


FIGURE 6 (*Right*). FLANGED RUBBER-LINED PIPE, FITTINGS, AND VALVES ON TOP OF A RUBBER-LINED STEEL STORAGE TANK

FIGURE 7 (*Left*). EIGHTEEN-INCH STEEL PIPE LINED WITH 5/16-INCH SPECIAL RUBBER FOR HANDLING HOT WASTE ACID FROM STEEL MILL PICKLING OPERATIONS

(Flexlock couplings at joints)

metal parts will conform to his specifications covering suitability for lining.

Valves must be specifically designed for rubber lining. It is best, therefore, to consult the manufacturer for recommendations. Figure 4 shows one of the standard rubber-lined valve designs, suitable for both pressure and vacuum service.

In any long pipe line, expansion and contraction are a problem. Short lengths of rubber hose can be installed at intervals to take care of these changes, or, preferably, special expansion joints can be specified, as shown in Figure 5. This has proved to be a very simple and efficient construction.

Figure 6 shows a typical assembly of rubber-lined pipe, fittings, and valves at the top of a rubber-lined steel storage tank for hydrochloric acid.

Flexlock Construction

A new type of flexible coupling for pipe lines has recently been made available and seems particularly adapted to the larger sizes of rubber-lined pipe in low-pressure or gravity-flow installations. In this construction, plain-end steel pipe is lined on the inside and the rubber is carried back about 5 inches on the outside at each end. A special ribbed, rubber gasket, known as Flexlock, is slipped over each end of two adjoining pipe lengths, and a split-steel rubber-lined sleeve is bolted over the two ends to make the seal. About $^1/_4$ inch of free space is allowed between pipe ends so that expansion and contraction in long lines are readily absorbed at the joints. The coupling assembly is sufficiently flexible to permit small angularities in the line without special fittings. Likewise, misalignment of pipe lengths can be compensated for within reasonable limits.

Figure 7 shows an 18-inch pipe line of this construction installed at one of the large steel mills to handle hot acid wastes from pickling operations. The pipe is lined with $^5/_{16}$-inch rubber of a special construction designed for severe service. Sudden variations in temperature, which caused previous pipe lines to fail, have had no adverse effect.

Practically all the worthwhile developments in this highly specialized field of rubber-lined equipment were brought about primarily as a result of far-sighted engineers in processing industries discussing their problems freely with rubber technologists. Frank and serious discussions between men of different industries cannot fail to bear fruit in new ideas.

[Translated for Rubber Chemistry and Technology from Kautschuk, Vol. 13, No. 3, pages 34–38, March, 1937.]

Contributions to the Analysis of Rubber

I. Determination of the Water-Soluble Components of Rubber

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Introduction

Investigations in the field of rubber analysis have neglected badly the determination of the water-soluble components of rubber. As a matter of fact, this determination was formerly of no great importance, because these substances are present in only very small quantities in ordinary plantation rubber. Today however, latex is finding application in the impregnation of fabrics and in the direct production of rubber goods, such as gloves and rubber thread. Furthermore an increasingly greater number of types of raw rubber, prepared by spraying or evaporation, are being produced, so that in general the determination of water-soluble components has become of more importance.

All the analytical methods which are to be found in the literature for determining water-soluble components depend on extraction with water. For example, in directions in one publication for analyzing rubber,[1] the following procedure is given: Extract for 10 minutes at least 10 grams of finely divided sample three times in succession with 5 times the quantity of water, filter, evaporate the filtrate, and dry the residue at 100° C. to constant weight. The result gives an approximate idea of the content of water-soluble components.

Exactly the same method is mentioned by Reiner,[2] Hauser,[3] and Dawson and Porritt.[4] L. E. Weber describes the following method. Extract 5 grams of finely divided sample with 100 cc. of water on a water bath for 5 hours, and repeat the process with the same quantity of water.

In the Government Rubber Institute at Delft, Holland, likewise, the rubber is extracted on a water bath, with the difference, however, that the first extraction is for 6 hours and the second extraction is for only 2 hours, with 50 cc. of water each time.

It was observed that the percentage of water-soluble components in evaporated latex is always too low. With normal latex, containing approximately 40 per cent of rubber, the difference in the rubber contents determined by evaporation and by coagulation, respectively, is 3 to 4 per cent. The content of serum substance of dried latex rubber is therefore 7 to 10 per cent. The content of water-soluble substances, however, has been found to be not greater than 4 per cent in most cases. Only in the case of very fresh samples has the value been greater than this. After storage of latex, and of rubber obtained by evaporation of latex, the percentage of water-soluble substances has, strange to say, been found to decrease gradually. A number of experiments were carried out by the methods discussed above. However, the time of extraction was lengthened, and besides this, the rubber was extracted with 0.5 *N* acetic acid as well as with water. The results are summarized in Table I.

TABLE I

WATER-SOLUBLE SUBSTANCES IN RAW RUBBER, DETERMINED BY VARIOUS METHODS

	Hot Extraction for 3 and 10 Min.	Water Bath 6 and 2 Hrs.	Hot Extraction 1 Hr.	Hot Extraction 6 and 2 Hrs.	Hot Extraction 6 and 2 Hrs. with 0.5 *N* Acetic Acid
(1) Evaporated latex	2.0	2.9	1.8	3.4	3.2
(2) Evaporated creamed latex	0.5	0.6	0.5	1.0	1.0
(3) Hopkinson rubber	0.8	2.0	1.2	1.2	4.0
(4) Kerbosch rubber	2.5	3.8	2.5	2.5	3.2

Samples (1) and (2) were evaporated at room temperature; the percentages of serum substances, calculated from the difference between the results of evaporation and of coagulation, were 7.5 per cent and 3.0 per cent, respectively. Sample (3) was prepared by spraying of latex by the Hopkinson process. Sample (4) was prepared by evaporation of latex by the Kerbosch process.

It is obvious from Table I that the serum substances were not completely extracted by any of the methods. By prolonging the times of extraction, somewhat higher values were obtained. The use of 0.5 *N* acetic acid in place of water gave no better results.

A few experiments were also carried out with vulcanized rubber prepared from four different samples of raw rubber, using the mixture: rubber 100, sulfur 5, diphenylguanidine 1, ZnO 3, vulcanized 20 minutes in an autoclave at 147° C. The water-soluble substances were determined by extraction for 6 and 2 hours on a water bath. The analytical data are summarized in Table II; for comparison the data on the raw rubber are included.

TABLE II

	Vulcanized	Raw Rubber
First latex crepe	0.6%	0.1%
Evaporated latex	0.8%	2.4%
Hopkinson rubber	0.6%	2.8%
Kerbosch rubber	0.7%	3.5%

In the vulcanized samples, the extracts consisted chiefly of diphenylguanidine. These results show that the serum substances in vulcanized rubber are not extracted at all.

Experiments were than carried out to ascertain whether a long extraction would give higher values. Evaporated latex was vulcanized in the mixture described above for 10 and 20 minutes at 147° C., and then extracted with acetone to remove diphenylguanidine.

Five grams of rubber were then extracted 4 times with 10 cc. of water on a water bath for 6 and 2, and 10 and 10 hours. The results are shown in Table III.

TABLE III

EFFECT OF LONGER TIME OF EXTRACTION

	Raw Rubber	Vulcanized Rubber	
		10 Min. at 147°	20 Min. at 147°
	%	%	%
After extraction for 6 and 2 hours	2.7	0.06	0.06
After extraction for 10 hours	0.9	0.04	0.04
After extraction for 10 hours	0.4	0.04	0.03

The results in Table III show that, even with prolonged extraction, the serum substances are not extracted from vulcanized rubber.

Consequently the analytical procedures already mentioned for determining

water-soluble substances give results for raw rubber which are too low, and which are valueless in general for vulcanized rubber. It was therefore desirable to improve these methods of analysis greatly.

A procedure for the determination of small amounts of inositol in brain and muscle tissue has been published by Young.[7] This involves extraction with a mixture of 70 parts of acetone and 30 parts of water for 6 hours on a water bath. When extraction is complete, the acetone is distilled off, and the residue is agitated with ether. The aqueous solution is purified further with mercuric sulfate, barium carbonate, etc., and finally is titrated with potassium mercuric iodide. Since the serum substances consist to a great extent of 1-methylinositol, the rubber mixtures mentioned above were analyzed by this method.

Five grams of finely divided samples were let stand overnight in the above-mentioned acetone-water mixt. (70:30), and were then refluxed on a water bath for 6 hours. The solution was filtered, the acetone was evaporated on the water bath, and the aqueous residue was shaken with ether. When evaporated and dried at 100° C., the final aqueous residue gave the water-soluble substances.

The analytical data are summarized in Table IV.

TABLE IV

WATER-SOLUBLE SUBSTANCES DETERMINED BY THE METHOD OF YOUNG[7]

Rubber	Raw State %	After Vulcanization %
First latex crepe	0.3	0.7
Evaporated latex	3.0	1.3
Rubber powder	4.6	0.7
Hopkinson rubber	Not determined	0.8

The extracts of the vulcanized samples consisted chiefly of diphenylguanidine.

The data in Table IV show that the serum substances in raw rubber are only partially extracted, and those in vulcanized rubber are not extracted at all by the method of Young.

The question then arises whether this failure to extract serum substances is a result of failure of the solvent to penetrate the rubber. To answer this question, another experiment was carried out. A two-gram sample of vulcanized rubber, already extracted with acetone, was refluxed in 50 cc. of petroleum (b. p. 230–260° C.) for 2 hours, the soln. was shaken several times with water and with an acetone-water mixture (70:30), the aqueous solution and the mixt. of acetone and water were evaporated, and were finally dried at 100° C. The following results were obtained.

	Water	Acetone-Water
First latex crepe	0.4%	0.3%
Rubber powder	1.3%	1.3%

This shows that it is impossible to remove the serum substances by agitation with solvents.

Development of New Methods, with the Use of Acids

It seemed possible that the reason why the serum substances are not recovered by extraction with water is because they become insoluble, perhaps partially so during drying of the latex and completely so after vulcanization. In favor of this theory is the observation that when a latex film, prepared by evaporation at room temperature, is heated, its content of water-soluble substances diminishes. It did not seem impossible, therefore, that the serum substances might be rendered soluble

again by heating with acids. With this in view the following experiments were carried out.

(1) Two grams of evaporated latex (prepared at room temperature) in 50 cc. of petroleum (170–200° fraction) were refluxed until the rubber component was dissolved. The solution was transferred completely, by means of 50 cc. of hot water, to a distilling flask, and the petroleum was removed by steam-distillation. The aqueous solution remaining in the flask was filtered and evaporated on a water bath. To remove the last traces of petroleum, the residue was taken up in water, filtered, again evaporated, and dried at 100° C.[8]

(2) Method (1) was repeated, except that, previous to steam-distillation, the petroleum solution was heated with 5 cc. of acetic acid for 30 minutes on a water bath.

(3) Method (1) was repeated, except that, previous to steam-distillation, the petroleum solution was refluxed with 5 cc. of acetic acid and 5 cc. of water for one hour on an oil bath. The temperature of the oil bath was around 120° C.

The following percentages of serum substances were found by the three methods:

Method (1) 2.1%
(2) 2.9%
(3) 4.2%

The results show that the serum substances are rendered soluble by heating with aqueous acetic acid. Accordingly the following modifications of the methods were made.

(*a*) Rubber extracted with acetone was employed, because in studying vulcanized rubber, removal of organic accelerators and free sulfur is desirable. As a control, though serum substances are also extracted with acetone, the acetone extract of dried latex was heated with 50 cc. of water on a water bath for 30 minutes and, after cooling, was filtered. The filtered solution was evaporated on a water bath and dried at 100° C. There was found 1.3 per cent of water-soluble substances in the acetone extract. The calculated content of serum substances was 7.5 per cent; therefore the content of water-soluble substances in the acetone-extracted rubber was 6.2 per cent.

(*b*) Xylene was employed as solvent, because complete distillation of the petroleum was difficult. The following experiments were carried out.

(i) Two grams of extracted rubber and 80 cc. of xylene were refluxed for several hours on a water bath, 5 cc. of acetic acid were added, the rubber was dissolved by refluxing on an oil bath, after complete solution 5 cc. of water were added, the solution was heated on the oil bath for 1 hour at 110–120° C., when cool the contents of the flask were transferred to a distillation flask, the first flask was rinsed with 50 cc. of water, the xylene was removed by steam-distillation, the residue in the flask was filtered, evaporated on a water bath, and dried at 100° C.

(ii) Two grams of extracted rubber were dissolved in xylene as in Experiment (i), were heated with water on an oil bath, 5 cc. of acetic acid and 5 cc. of water were added, the solution was heated on a water bath for 2 hours, with frequent agitation because of the rapid formation of 2 layers, and the solution was steam-distilled as in Experiment (i).

(iii) Two grams of extracted rubber were heated with 80 cc. of xylene and 5 cc. of acetic acid on a water bath until the rubber was completely dissolved, 5 cc. of acetic acid and 10 cc. of water were added, and the solution was heated for 4 hours longer on the water bath. Here too the solution was agitated frequently. It was then steam-distilled, as in Experiments (i) and (ii).

The following percentages of water-soluble substances were found:

Method (i) 4.0%
(ii) 6.1%
(iii) 6.2%

It is obvious that in methods (ii) and (iii) the serum substances are completely dissolved by heating with acetic acid and water. Heating on an oil bath is not necessary for determining the water-soluble substances in raw rubber, and solution and heating can be carried out satisfactorily on a water bath.

Method (ii) or (iii), henceforth designated as the steam-distillation method, gives therefore an improved means for determining the water-soluble substances in raw rubber. A number of samples of raw rubber were accordingly analyzed by Method (ii). The analytical results are summarized in Table V.

TABLE V

WATER-SOLUBLE SUBSTANCES IN SAMPLES OF RAW RUBBER

	Rubber	Percentage in Acetone Extract (*a*)	Percentage in the Extracted Rubber (*b*)	Sum *a* + *b*	Percentage by Old Method*
1.	First latex crepe No. 364	0.3	0.8	1.1	0.2
2.	First latex crepe No. 367	0.3	0.7	1.0	0.2
3.	First latex crepe No. 372	0.2	0.7	0.9	0.1
4.	First latex sheet No. 357	0.3	0.9	1.2	0.3
5.	First latex sheet No. 365	0.2	0.9	1.1	0.2
6.	First latex sheet No. 375	0.2	0.8	1.0	0.2
7.	Hopkinson rubber (1)	0.8	4.0	4.8	1.4
8.	Rubber powder (2)	2.3	5.7	8.0	4.4
9.	Rubber powder (3)	2.4	5.5	7.9	4.0
10.	Dried latex (4)	1.3	6.3	7.6	2.9
11.	Dried concentrated latex (5)	0.7	2.2	2.9	0.5
12.	Dried concentrated latex (6)	1.0	3.0	4.0	1.3
13.	Dried concentrated latex (7)	0.5	1.1	1.6	0.1
14.	Dried latex (8)	1.8	9.9	11.7	7.9
15.	Dried latex (9)	1.7	8.8	10.5	6.8

* See Table I, column 2.

(1) After 8 years' storage.
(2) and (3) Prepared by spraying latex.
(4) Latex over one year old.
(5) Concentrated by creaming.
(6) and (7) Concentrated by centrifuging.
(8) and (9) Samples from young clones.

The data in Table V lead to the following conclusions.

(1) Part of the serum substances is extracted by acetone. It should however be noted that acetone extraction is not necessary in determining the serum substances in raw rubber.

(2) The steam-distillation method gives much higher percentages of water-soluble substances than does the old method.

(3) Ordinary types of plantation rubber, *i. e.*, first latex crepe and sheet, contain approximately 1 per cent of serum substances, whereas the old method never indicates more than 0.1 to 0.3 per cent.

(4) Samples of normal, dried latex, such as Samples 8, 9, and 10, contain 7 to 8 per cent of serum substances, amounts which agree with the calculated values.

(5) Latices obtained by creaming and by centrifuging contain lower percentages of serum substances, as is evident from the values shown for Samples 11, 12, and 13. This agrees completely with all known facts about the concentration process.

(6) Dried latex from special clones (Samples 14 and 15) contains relatively high percentages of serum substances, and therefore the latices are of unusual composition.

In brief then, it may be concluded that the newly developed method gives correct values for the content of water-soluble components in raw rubber.

Determination of Serum Substances in Vulcanized Rubber by the New Method

Samples of raw rubber, including first latex crepe, first latex sheet, evaporated latex, Hopkinson rubber, and rubber powder were vulcanized in the form of mixtures of rubber 100, sulfur 5, diphenylguanidine 1, and zinc oxide 3, at 147° C.

The water-soluble substances were determined by Method (ii), which was developed for raw rubber.[9] Since, however, zinc oxide was dissolved by the hot acetic acid, the water-soluble substances were, after evaporation to dryness, redissolved in water and the zinc compounds were precipitated with hydrogen sulfide, were filtered, the filtrate was evaporated, and dried at 100° C. The results of these determinations are summarized in Table VI.

TABLE VI

WATER-SOLUBLE SUBSTANCES IN VULCANIZED RUBBER

Mixing	Time of Vulcanization (Minutes)	Percentage in Acetone Extract	Percentage after Acetone Extraction
First latex crepe No. 372	Unvulcanized	0.8	0.8
First latex crepe No. 372	20	0.7	1.0
First latex sheet No. 375	Unvulcanized	0.7	0.8
First latex sheet No. 375	20	0.6	0.9
Evaporated latex	Unvulcanized	1.2	5.8
Evaporated latex	10	1.4	5.6
Evaporated latex	20	1.5	5.4
Hopkinson rubber	Unvulcanized	0.9	5.1
Hopkinson rubber	10	1.3	5.2
Hopkinson rubber	20	1.2	5.0
Rubber powder	Unvulcanized	1.6	5.6
Rubber powder	10	1.0	5.9
Rubber powder	20	1.0	5.5

Two general conclusions may be drawn from the results shown in Table VI.

(1) The water-soluble substances in vulcanized rubber can be determined correctly by the new method of analysis, as is evident from a comparison of the values for the unvulcanized mixtures with those of the corresponding vulcanized mixtures. It is to be noted that part of the unconsumed diphenylguanidine is present in the water-soluble portion of the acetone extract, so that the water-soluble substances of vulcanized rubber do not consist exclusively of serum substances originating from the rubber in the vulcanizate.

(2) Here too a considerable difference is evident between the values for first latex crepe and sheet and for the same mixtures with evaporated (whole) latex.

Influence of Glue

To ascertain the effect of glue the following mixtures were vulcanized 20 minutes at 147° C.

	A	B	C
First latex sheet	100	100	100
Sulfur	3	3	3
Diphenylguanidine	1	1	1
Zinc oxide	5	5	5
Plastoleim (glue)	7.5	14.5	...
Bone glue	...	...	9

Each of the three vulcanized mixtures was analyzed for:

(*a*) Water-soluble substances in the acetone extract:

(*b*) Water-soluble substances in the acetone-extracted vulcanizate, by the steam-distillation method, after precipitation of zinc as zinc sulfide.

(*c*) Water-soluble substances in the vulcanizate (not acetone-extracted) by the old method.

The analytical results are summarized in Table VII.

TABLE VII

WATER-SOLUBLE SUBSTANCES IN MIXTURES CONTAINING GLUE

	(a)	(b)	(c)
Vulcanizate A	0.4	2.3	1.0*
Vulcanizate B	0.4	2.9	0.8*
Vulcanizate C	0.4	1.9	0.2*

* The extract contained diphenylguanidine.

These results show that only a small part of the glue is dissolved by the steam-distillation method, and almost none by the old method.[10]

Glue in the water-soluble substances isolated by the steam-distillation method was detected by means of tannic acid. The attempt was then made to separate the glue by means of aqueous lead acetate. To this end the extract was evaporated, taken up in water, 3 cc. of 10 per cent aqueous lead acetate added, let stand for 0.5 hour, filtered, the lead in the filtrate precipitated by hydrogen sulfide, the filtered solution again evaporated, the residue dried at 100° C., the ash content of the extract determined and calculated to a basis of the whole mixture. The analytical results are summarized in Table VIII.

TABLE VIII

WATER-SOLUBLE SUBSTANCES AFTER TREATMENT WITH LEAD ACETATE

Mixture	Water Soluble Substances Without Lead Acetate	With Lead Acetate	Percentage Ash
Mixture A	2.3	1.3	0.5
Mixture B	2.9	1.4	0.5
Mixture C	1.9	1.5	0.5
Evaporated latex vulcanized	5.6	4.2	1.0
First latex crepe No. 372 vulcanized	1.0	1.0	0.2
First latex sheet No. 375 vulcanized	0.9	0.9	0.2

The data in Table VIII show that glue is completely removed, and that part of the serum substances are lost by treatment with lead acetate.

Influence of Calcium Compounds and Magnesium Compounds on the Determination of Water-Soluble Substances

In determining water-soluble substances by the new method, any calcium and magnesium compounds which are present in the rubber mixtures are converted into acetates, and consequently are falsely determined as water-soluble substances. Therefore to obtain a correct value of the water-soluble substances, it is necessary to remove these acetates. Experiments were accordingly carried out to accomplish this.

A series of four mixtures were prepared from first latex crepe and evaporated latex and these mixtures were vulcanized 20 minutes at 147° C.

	D	E	F	G
Rubber	100	100	100	100
Sulfur	5	5	5	5
Diphenylguanidine	1	1	1	1
Zinc oxide	3	3	3	3
Calcium oxide	..	5	..	5
Magnesium oxide	..	..	5	5

The water-soluble substances in the vulcanizates were first determined by the new method, and were then treated with lead acetate. In this way the zinc salts in the solutions were removed. The following method was developed for removing calcium acetate and magnesium acetate.

Calcium.—After treatment with lead acetate and elimination of the lead, the solution was freed of hydrogen sulfide by boiling, was made alkaline with ammonium hydroxide, 10 cc. of 10 per cent ammonium carbonate solution were added, the solution was heated on a water bath for 1 hour, the precipitate was filtered off, the filtrate was evaporated, the residue was taken up in a little water, 5 cc. of 10 per cent ammonium carbonate solution were added, and the solution was heated on a water bath for 0.5 hour. If calcium carbonate still precipitated, it was filtered, the filtrate was evaporated on a water bath, the residue was taken up in water, the solution was evaporated to dryness the process was repeated until the ammonium salts were completely eliminated, and finally the product was dried at 105–110° C. for 2 hours.

Magnesium.—After removal of calcium acetate by ammonium carbonate, the residue was dissolved in 50 cc. of water, the solution was heated to boiling, 10 cc. of ammonium stearate solution (prepared by dissolving 5 grams of stearic acid in 100 cc. of warm 5 per cent aqueous ammonia) were added, the solution was heated on a water bath for 1 hour, was cooled, filtered through a Gooch crucible, the residue was washed with water, the filtrate was evaporated, the residue taken up in water, again evaporated to dryness, the process was repeated, and finally the residue was dried at 105–110° C. for 2 hours.

The analytical results are summarized in Table IX.

TABLE IX

DETERMINATION OF THE WATER-SOLUBLE SUBSTANCES IN VULCANIZED RUBBER AFTER ELIMINATION OF ZINC, CALCIUM, AND MAGNESIUM COMPOUNDS

	Mixture	Percentages D	E	F	G
First latex crepe mixtures	Untreated	4.5	16.7	21.2	30.5
	Treated with lead acetate	1.1	11.4	14.5	23.1
	Treated with ammonium carbonate	1.1	1.7	..	9.9
	Treated with ammonium stearate	1.3	..	1.7	1.7
Evaporated latex mixtures	Untreated	8.4	22.0	23.5	31.5
	Treated with lead acetate	4.5	14.7	18.0	27.0
	Treated with ammonium carbonate	4.7	5.4	..	12.0
	Treated with ammonium stearate	4.5	..	4.4	4.0

The results in Table IX show that calcium is almost completely eliminated and magnesium is completely eliminated by the proposed method. The analytical results on the mixtures of first latex crepe and evaporated latex are sufficiently different to make it possible to decide whether a mixture has been prepared from ordinary plantation rubber or from evaporated latex.

Influence of Textile Fabrics

To ascertain the influence of textiles on the determination of water-soluble sub-

stances by the steam-distillation method, canvas was analyzed by this same method. The results were as follows:

Water-soluble substances	2.5%
Water-soluble substances, treated with lead acetate	1.7%*
Ash content of the water-soluble substances	0.9%

* This extract consisted chiefly of acetates.

These values show that textiles give rise to two errors:

(1) the formation of water-soluble substances, which however are eliminated by lead acetate.

(2) the formation of acetates.

The facts described above show that the steam-distillation method is complicated by the presence of glue, calcium compounds, magnesium compounds, and textiles. When the method is applied to vulcanized rubber goods, qualitative tests for the presence of these materials should first be made. If only zinc is present, it can be removed as zinc acetate by means of hydrogen sulfide.

When glue and textiles are present, treatment with lead acetate is necessary. On the other hand, if glue and textiles are absent, any calcium acetate or magnesium acetate which may be present can, after elimination of zinc by hydrogen sulfide, be removed by the proposed method.

Summary

1. It is shown that the methods which are ordinarily used for determining water-soluble substances in raw rubber give low results, and are quite useless for vulcanized rubber.

2. New analytical procedures are developed for determining the water-soluble substances in raw rubber and in vulcanized rubber. These procedures are carried out in the following manner.

(*a*) *Raw Rubber.*—Heat 2 grams of rubber in 80 cc. of xylene and 5 cc. of acetic acid on a water bath until the rubber is co npletely dissolved, add 5 cc. of acetic acid and 10 cc. of water, heat for 3–4 hours on the water bath with frequent agitation, transfer to a distilling flask (rinsing the first flask with 50 cc. of hot water), distill the xylene with steam, filter the residual solution, evaporate the filtrate on a water bath; and dry at 100° C.

(*b*) *Vulcanized Rubber and Rubber Mixtures.*—First extract the sample with acetone, heat 2 grams of the acetone-extracted sample with 80 cc. of xylene on a water bath, add 5 cc. of acetic acid, reflux the mixture on an oil bath, after complete dissolution add 5 cc. of acetic acid and 10 cc. of water, heat the solution for 2 hours on an oil bath at 110–120° C., distill the xylene, as in the determination with raw rubber, filter the residue, evaporate the filtrate to dryness, take up the residue in 50 cc. of water, pass a current of hydrogen sulfide through the solution for 10 minutes to precipitate zinc as sulfide, filter, evaporate the filtrate, and dry the residue at 100° C.

3. In the presence of calcium compounds, magnesium compounds, glue and textiles, the method gives false results. Modifications of the method are therefore recommended, whereby these substances are eliminated.

The author wishes to offer his heartiest thanks to Dr. A. van Rossem, Director of the Institute, for his valuable aid in carrying out the work.

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[8] This method is similar to that used by Roberts (*J. Rubber Research Inst. Malaya*, **7**, 46 (1936)). It was published after the present investigation was completed.

[9] Later it was found that heating on a water bath with frequent agitation is unnecessary if the heating on the oil bath is prolonged and sufficient acetic acid and water are present. This modification in the method is mentioned in the Summary.

[10] The determination of glue will be described in a later communication.

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Physical Testing of Latex Films

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Introduction

Determinations of the tensile strength of latex rubber involve difficulties which concern either the preparation of the sheets or the technic used in breaking them. Thick sheets of latex rubber may be cut into dumb-bell or ring test-pieces, which may then be broken on a tensile-testing machine of normal type. The preparation of thick sheets is, however, a matter of difficulty, owing to the fact that the complete drying-off of the water takes such a long time. Thus when ultra-accelerators are under test, vulcanization of the sheets may be advanced, or even complete, before the sheets are dry, so that investigation of the early stages of cure is impossible. Further, during the time that elapses before evaporation has gelled the whole thickness of latex, sedimentation of the compounding ingredients may occur in the mass of the fluid sheet, resulting in vulcanizates which are not uniform in composition or degree of cure. The use of devices such as porous tiles or the expedient of flowing the latex onto the surface of a gelatin jelly is objectionable because they absorb water-soluble components as well as water from the latex mix. Further, although they tend to prevent sedimentation by promoting more rapid gelling, the complete elimination of the water from a thick sheet is still a lengthy process, during which complete self-vulcanization may easily occur. The use of chemical coagulants is open to the same objection, which is of course overshadowed by the much more serious obstacle of their effect on the activity of accelerators and on the physical properties of the latex rubber.

Sedimentation may also be avoided, though without marked reduction in the time of drying, by the addition of thickening agents. However, as a general principle it may be stated that once the latex technologist has decided to test a given compound (consisting frequently only of latex plus vulcanizing ingredients) he does not wish to complicate his problem and obscure the issue by adding any further ingredients.

It is not permissible to build up thick sheets by alternate processes of dripping and drying. Such sheets are not physically homogeneous, and their laminated structure leads to modifications and irregularities in their tensile strength.

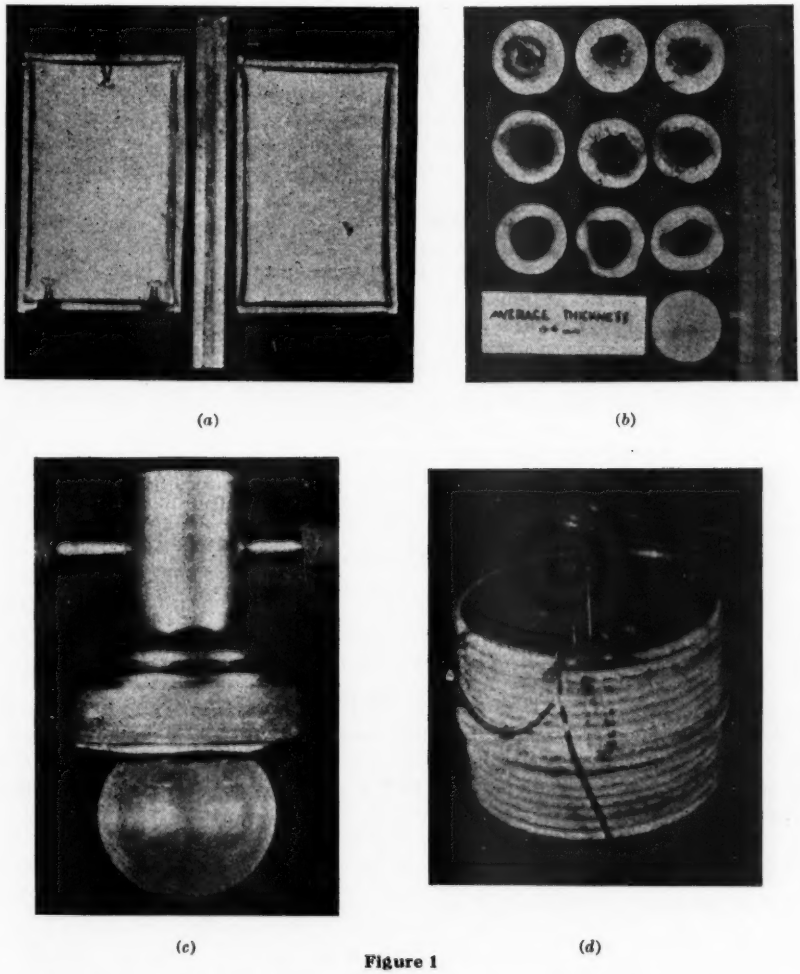
The foregoing considerations do not apply to cases where the tests are intended to control the quality of thick latex rubber articles in manufacture. Here one employs a simple modification of the manufacturing process to prepare plane sheets, and then tests a rubber which has the same properties as the articles under review. These considerations do, however, concern those who are engaged in research work in the compounding of latex rubber, or the development and manufacturing control of latex accelerators.

Thin sheets of latex rubber are simply and rapidly prepared by flowing and drying the latex on flat surfaces; no additions need be made to facilitate their preparation, and the period required for spontaneous setting is so short that sedimentation need not be feared.

Unfortunately, difficulties are encountered when attempts are made to determine the tensile strength of such thin sheets by the standard methods. It is found that determinations tend not to be reproducible within any acceptable margin of error and that this tendency is more seriously developed in under-vulcanized samples.

From half a dozen results on the same sample it may prove impossible to select a group capable of yielding a valid average, and the application of normal selection laws (*e. g.*, taking the average of the highest two of a group of six) results in a tensile strength-time curve of a most irregular type.

The source of error can be traced to the imperfect edges of test-pieces cut from these thin sheets. These tiny flaws may each start a tear at a high degree of elonga-



(*a*) (*b*)

(*c*) (*d*)

Figure 1

tion, and although such tears speedily fork in the direction of elongation, owing to the lines of cleavage formed by the aligned macro-molecules of the rubber, the effective cross section of the test-piece is reduced to a varying extent. Thus irregularly low results are obtained.

With ring test-pieces stamped from thin sheets, even the higher cures give hopelessly irregular results. Dumb-bell test-pieces, owing doubtless to the more restricted length of cut edge where these flaws can develop into tears, prove fairly

satisfactory for fully cured and semi-cured rubber, provided that the cutting knife is maintained in perfect condition and carefully lubricated. Under-cured and uncured latex rubber cannot be handled, even with the precautions just indicated.

The writers have devised a satisfactory technic by which dumb-bell test-strips of acceptable regularity may be obtained from thin sheets of latex rubber, but the method is not yet suitable for routine use. Before this method was available, a tensile test was sought in which the difficulties would be avoided by having no free cut edges exposed to elongation. In other words, a satisfactory bursting test was required.

The method selected was the very obvious scheme of clamping the sheets of rubber tightly between two rings and bursting the central portion by means of fluid pressures. No novelty is claimed for the basic idea, but the writers do claim to have established the method on a sound basis, and to have shown how the resultant observations may be used to calculate values which have both practical and theoretical significance.

A matter which was kept steadily in view during this investigation was the cost of the apparatus. The writers are fortunate enough to have access to the most modern physical testing equipment, but they recognize that the high cost of this equipment must restrict seriously the output of work on the tensile strength of raw and vulcanized latex films. Latex work in many firms is in a preliminary stage, where the caution proper to a well-run business would forbid heavy expenditure on laboratory apparatus. In other cases, the total amount of work to be done, or the staff available, could not make enough use of a standard tensile-testing machine for its purchase to be a sound economic proposition, even though ample funds might be available. Lastly, there are cases where such a machine would be out of place through unsuitable local conditions and lack of facilities for erecting and maintaining it. The writers have in mind tensile-testing in plantation countries. The apparatus used for this bursting test (1) is simple and strong, (2) need not be erected as an engineering job, and (3) costs no more than a few pounds.

Thus the advantages claimed for this bursting test, proposed as a means of determining the tensile strength of latex films, are that it yields more regular and reliable results than the standard method of tensile-testing, and employs apparatus of only a fraction of the cost. The tests are as quickly carried out.

The Method in Practice

The film-bursting test is a method of determining the tensile strength and elongation at rupture of thin sheets of latex rubber by observations taken when the central portion of a test-disc is blown up to bursting point. The tensile strength is calculated by the formula:

$$T = \frac{Pr^2}{a\,b}$$

where T = tensile strength in kg. per sq. cm.

P = the fluid pressure (kg. per sq. cm.) which actually bursts the disc.

r = the radius in cm. of the bubble at the moment of burst. This value is $\sqrt[3]{\frac{3V}{4\pi}}$, V being the volume of the bubble.

a = the radius in cm. of the aperture exposing that portion of the test-disc which is free to expand.

b = the thickness in cm. of the test-disc before inflation.

E_B = the elongation at break, is given by the formula $E_B = \frac{2r}{a}$.

The following method of preparing the sheets was found to be satisfactory. Rectangular pieces of stout window glass, 9 inches by 5.75 inches, are carefully cleaned. Gummed strips of brown paper are folded along their length, and then stuck on to the edges of the glass plates to convert them into shallow trays (Fig. 1*a*). A suitable quantity (*e. g.*, 20 cc.) of the mix under test is poured onto such a plate, which is manipulated by tilting to distribute the latex as a uniform film. The plate is then placed on a level table, which merely consists of a good piece of plate-glass supported on three screws of adjustable height. Enough plates for the work in hand are poured rapidly, and when all are on the levelling table the latter is covered by sheets of cardboard bent into semi-cylindrical shape. Finally, the two ends of the cardboard hood are covered with wet muslin, whose function is to retard the initial stages of drying in the thin films and thus avoid the cracking or other surface irregularities which otherwise frequently occur. Under these conditions, at average laboratory temperature, the sheets are found to be perfectly dry after 24 hours and go at once for vulcanization. The whole arrangement is shown in Fig. 2.

Experience as well as theoretical considerations showed that the use of an ordinary thermostatically controlled air oven would lead to gross irregularities in the

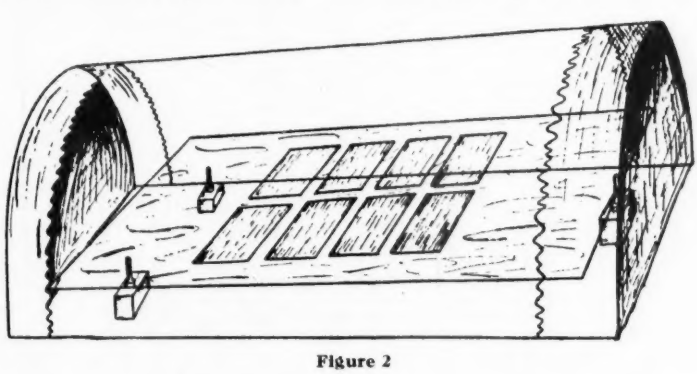


Figure 2

temperature of curing. Apart from the disturbance accompanying each opening of the door and the irregular radiation from the sides of the oven on the plates, the actual air temperature varies to an intolerable degree from point to point. A system was therefore evolved by which the rubber sheets, still on their glass plates, are vulcanized in narrow metal sheaths or pockets which dip into a thermostatically controlled circulating oil bath (Fig. 1*d*). The pockets are wide enough just to take the plates, and of such depth that the top of the plate is an inch or so below the oil level which comes to within about two inches of the top of the sheaths. Each sheath has its own lid. The plates are fitted with three spring paper clips which are triangular in cross section and are of a total width just admitted by the pockets. These serve to keep any part of the glass plate from direct contact with the metal sides of the pocket. Vulcanization is thus effected partly by radiation and partly by contact with the hot air. Actually, there is a negligible difference between the air temperature inside the sheath and the oil temperature outside. One of the spring clips carries a ring by which the plate is withdrawn from its pocket when cure is complete.

Figure 3 shows the cylindrical oil bath, together with the basic circulating device, which comprises an inner cylinder raised from the bottom of the drum and reaching

to within about 0.5 inch of the surface of the oil. A long-bladed propellor works near the bottom of this inner cylinder, and immediately above is placed a false bottom of coarse metal gauze which serves to equalize the intensity of circulation. The oil is pushed up and flows over the top of the cylinder and down the outside to the inlet at its base. The outer container is heavily lagged, and is heated by means of a large gas ring controlled by an all-metal thermostat immersed in the oil.

A system of twelve pockets is superimposed on this device. They radiate like the spokes of a wheel from a closed and stationary cylinder, which carries the bearings for the propellor shaft and reach to the inner cylinder to which they are attached. The whole system is effective in maintaining a uniform circulation of oil at uniform temperature around the whole surface of the pockets with the exception

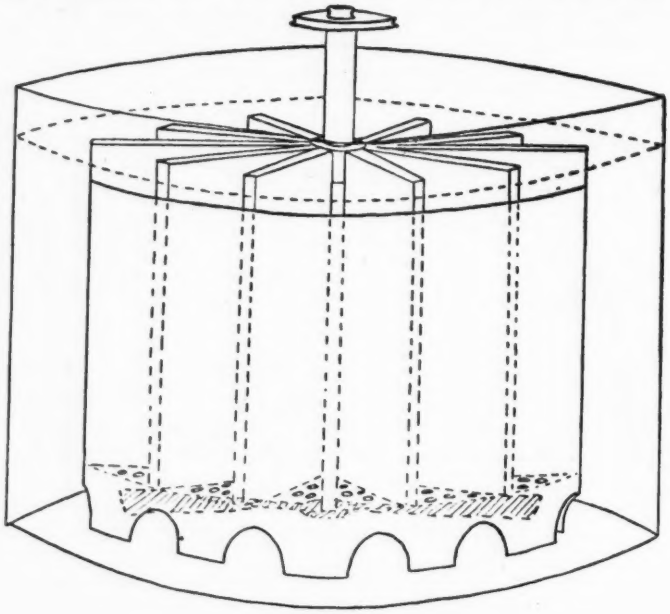


Figure 3

of a small upper fraction of their length. As already mentioned, the rubber films are well below the oil level for their entire length.

After vulcanization, the plates are allowed to cool, and the films are then chalked and stripped off. Actually the gummed strips come off at the same time, serving as a frame to the rubber film, and there is no distortion even of uncured sheets. A cutting machine carrying a 1.75 inch diameter knife is then used to stamp out the test-discs.

Initially, the thickness of the disc was measured with a micrometer gage, but it was soon found that it was more satisfactory to weigh it on a chemical balance, calculating the thickness by means of a factor based on the diameter and the density of unloaded vulcanized rubber of low sulfur content. With sheets varying from 0.2 to 0.4 mm. in thickness, it is evident that weighing must give a more reliable figure than a direct measurement, apart altogether from the slight compression due to the nip of the gage. Measured results are generally lower than those calculated from a weighing, presumably for the reason just indicated.

The convenient term of "bursting die" was adopted to describe the apparatus used for holding the rubber. It consists of a small cylindrical chamber of gun-metal, plugged at one end and closed at the other by a plate carrying a central hole half an inch in diameter. The outer face of this plate carries two short pins which serve to center two stout metal washers, the lower carrying a central 0.5 inch diameter hole, and the upper carrying a central 1 inch diameter hole. The test-disc of thin rubber 1.75 inch in diameter is then placed between these washers, which are then clamped tightly in position by screwing down a stout cap, also with a central 1 inch diameter aperture. Two short inlet pipes to the chamber serve, respectively, as leads for applying fluid pressure and measuring the said pressure by means of a simple mercury manometer. Evidently a central circle one-inch in diameter of the test-disc is free to be inflated by the applied pressure. A workshop drawing of the "die" is shown in Fig. 4, and it also appears in Fig. 1*c*.

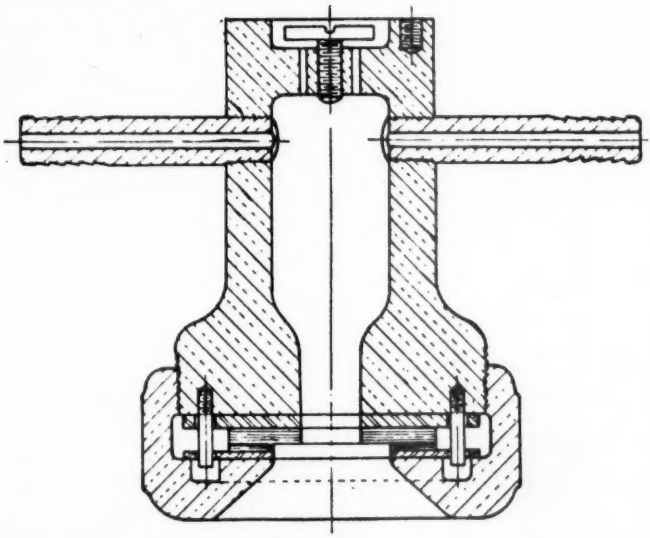


Figure 4

Attention was first directed to the use of water pressure instead of compressed air to furnish the fluid pressure. Under normal conditions, the high pressure of the water main is always available. In isolated surroundings, high water pressure can always be obtained very easily by other means, *e. g.*, displacing water from a bottle by running in mercury from a reservoir placed several feet higher. The mercury method of securing pressure could also be adapted to the bursting of films with and in liquids other than water; further, the liquid could be used at temperatures higher than the atmospheric normal. The apparatus used for operating this test by water pressure is shown in Fig. 5. In this case the entire system comprising the interior of the die, the lead from the water main, and the manometer lead as far as the actual mercury surface which takes the pressure, is kept filled with water. The die simply hangs across the mouth of a tin container which is previously filled with water, the die aperture closed by the test-piece being fully immersed; any excess of water runs out of an overflow pipe. When the flow has ceased, an empty vessel is placed under this spout, and the water pressure is turned on. Thus the disc is inflated with water, in water, and the water displaced is collected as it flows from the

spout. When the slight click of the break is heard, the water tap is at once closed. Thus the volume of water collected from the overflow spout should represent the volume of the bubble at burst. Experiment has shown that if the tap be closed with normal celerity, the excess of water which flows from the tap after rupture has started does not exceed 5 per cent of the volume of the bubble, representing an error in the calculation of its surface measurement of not more than 3 per cent.

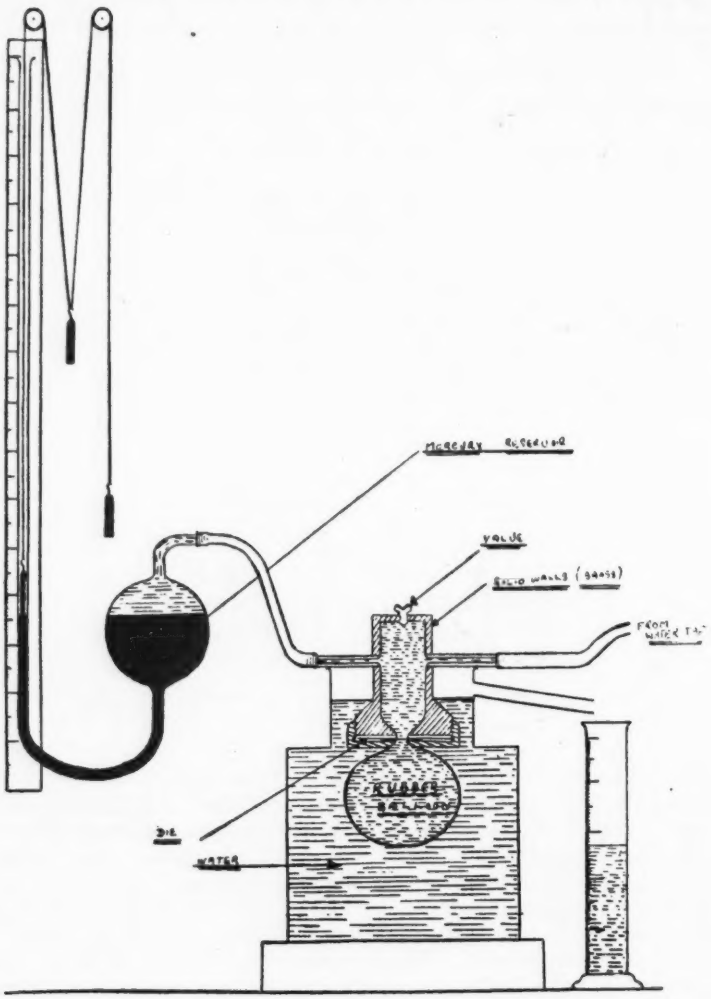


Figure 5

The method is quiet, surprisingly little disturbance occurs at the moment of break owing to the low compressibility of water, and for the same reason accidental bursts in other parts of the equipment would be without serious danger.

A simple modification, which is already shown in the detailed illustration of the die (Fig. 4), was required, for to avoid slipping of the test-disc, the washers must be

dry when the disc is inserted. When the die is inverted for this purpose, it is not entirely full of water, and a certain amount of air is thus shut in under the disc. On replacing the die on the mouth of the container, this air collects at the closed end of the die, and is expelled through a small screw valve without inflating the disc by turning on a slow stream of water.

Figure 5 also shows the manometer, which needs only brief notice. The manometer has a large reservoir in which the mercury surface takes the water pressure: thus a considerable rise in the mercury column has little influence on the manometer zero point. The manometer reading required is evidently the maximum reading obtained, as pressure rises steadily during the latter part of the inflation. A simple height-recording device used with success consists of a glass plunger resting on the mercury surface in the manometer tube; the plunger hangs on a thread, which, when it leaves the open tube, passes over a pulley and then supports a counterpoise weight.

It is noted that when the pressure is first turned on, the manometer rises rapidly with but little overflow of water from the spout of the container. A yielding point is then reached at which inflation begins, and the mercury drops slightly, and then

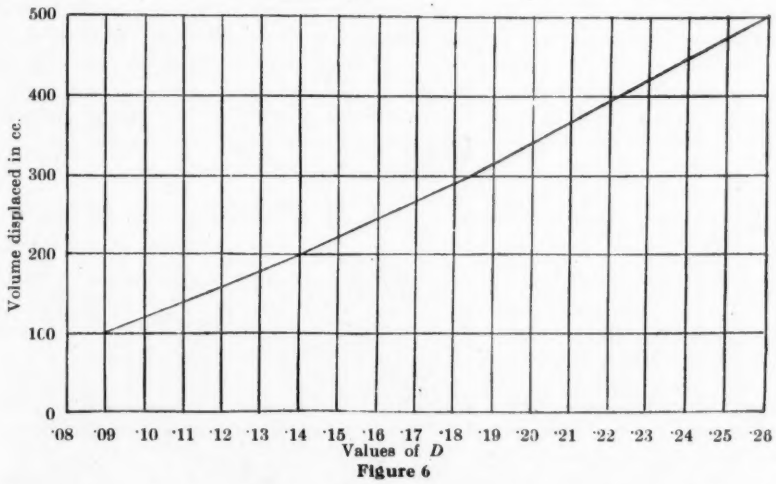


Figure 6

starts to rise steadily to a much higher maximum value. Figures of the order of 40 to 50 centimeters of mercury are obtained with well-cured latex rubber sheet of the normal order of thickness of from 0.2 to 0.4 mm. The volume of the bubble at break is usually of the order of 400 cubic centimeters.

The formula may be written $T = \frac{r^2}{a} \times \frac{P}{b}$.

Even assuming the bubble to be a perfect sphere, the calculation of r from V, the volume at burst, is a troublesome operation to perform when computing a long series of tensile results. This difficulty may be overcome by use of a graph (Fig. 6).

For a given "die" a is a constant; r may be calculated from V, the volume of the bubble at burst. Thus, values of V can be graphed in terms of $\frac{r^2}{a}$, and for any value of V, the corresponding value of $\frac{r^2}{a}$ which is called D, may easily be read.

The graph actually used gives a D value which incorporates the factor converting cms. of mercury into kg. per sq. cm. Thus in practice, $T = \frac{P'}{b} \times D$, when P' is the pressure in cms. of mercury.

The shape of the test-discs after bursting is similar for the air and water method and is of great interest. Good bursts on well-cured discs give a clean circle from which thin undistorted petals of rubber radiate inwards in a flower-like effect. With the lower cures, where the rubber has much permanent set, the petals are wider, longer, and distorted, and there is a sort of raised rim to the circle. With uncured sheets, only this rim remains. It appears that the stage of cure at which the thin undistorted petals first appear is that at which permanent set becomes negligible; in other words, the stage at which the technical cure is reached. A selection of burst discs will be found in the photograph (Fig. 1*b*).

It may be seen that, just as uni-dimensional elongation causes an orientation of the rubber molecules in the direction of stress, so the inflation of a disc into a bubble will cause a radial orientation of the molecules towards the pole of the bubble. The further one travels from the pole of the bubble, the more pronounced will be this orientation, which amounts to an alignment of the molecules along the lines of longitude of the spheroid. Now in vulcanized rubber, the hydrocarbon chains which constitute the molecules are furnished with cross-linkages provided by sulfur atoms, their number increasing with the degree of vulcanization. Sulfur linkages are known to be brittle. Thus, in a bubble from rubber of any considerable degree of vulcanization, one would expect the lines of longitude to be lines of cleavage in the case of break, giving to the burst disc a petal-like structure. This, as has just been stated, is actually observed in practice.

In a subsequent section it is pointed out in greater detail that the bubbles burst by failure at the pole where the rubber is thinnest. It will thus be realized that the force actually measured is the force required to break the end-to-end cohesion of the molecules, just as in the case of breaking a dumb-bell by uni-dimensional pull. Only after rupture has occurred does the rubber tear down the lines of weakness between the chains.

Incidentally, it may be remarked that a bad break or a slip can be detected from the irregular appearance of the burst disc. Further, a bad break usually modifies the sharp click of bursting, and slips cause a hesitation in the rise of the mercury column and may even produce actual fluctuation.

In practice, and particularly when the water-pressure method was employed, slipping of the test-disc in the die proved initially to be extremely difficult to control. Washers of rubber and rubberized fabric and complicated systems of abrasive and interlocking washers all proved unsatisfactory, as did the use of a flange at the upper washer opening to limit accurately the size of rubber free to expand. Finally, success was achieved by using a soft, well-vulcanized rubber facing to the washers, drying this carefully before use, and then wiping over with a rag moistened with benzene before applying the test-piece.

Evidently it was of importance to consider how such slip would influence the results obtained. At the same time, the other possible type of accident, a bad break due to a flaw in the film, was also investigated.

Now $T = \frac{E_B^2 Pa}{4b}$ and for a given sheet of rubber at a given cure, T and E_B are fixed values, so that $\frac{P}{b}$ varies with $\frac{1}{a}$.

But b, the thickness of the disc, cannot be affected by slip in the die, the only ef-

fect of slip being to give a a greater value than that used in the calculation. As a is increased, P is diminished in proportion. If the disc slipped in the die during inflation, this would lead to a low value of $\frac{P}{b}$.

From $E_B = \frac{2r}{a}$ it follows that slip would give fictitiously high values for r and hence for D. A bad break would also occur at a low value of $\frac{P}{b}$, but the break would occur too soon, *i. e.*, at a low value for r and hence at a low value for D.

In investigating a series of test-pieces from a sheet of rubber of uniform cure, $\frac{P}{b}$ and D should each be constant. Any low values for $\frac{P}{b}$ might indicate either slip or

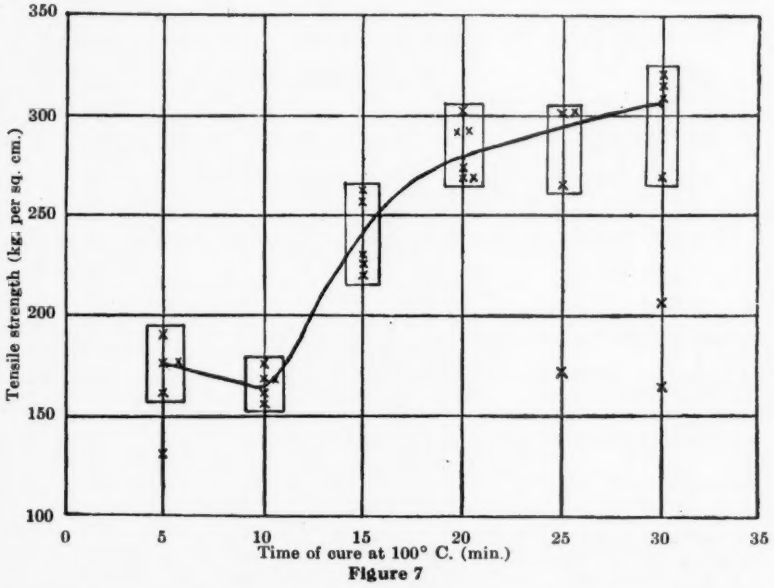


Figure 7

a bad break but the cases would be distinguished by an inspection of the D values. Abnormally high values for D would indicate slip while low D values would indicate bad breaks.

It is usual to burst 6 discs from each sheet of rubber, *i. e.*, from each period of cure. Of these, some may be lost by bad breaks. It is important to convey some idea of how the several figures obtained from each cure agree among themselves, and to indicate the method used in selecting the final figure which is taken as the tensile strength at a given cure. Figure 7 shows, on a tensile strength-time curve, how the various results for each cure are scattered. In practice, one takes the highest tensile figure, and all within 15 per cent of this figure, and uses the average. Should the highest figure include an inadequate number of the other figures within the 15 per cent limit, it is rejected as fictitious, and the next figure is taken. The figures which fall within the 15 per cent group are indicated on the graph shown in Fig. 7 by an oblong enclosure. These values were obtained by the water-bursting

method. A commercial ammonia-preserved centrifuge concentrated latex of 60 per cent rubber content was compounded with 50 per cent dispersions of sulfur and zinc oxide, and with a concentrated aqueous solution of diethylammonium diethyldithiocarbamate to give a mix consisting of rubber 100, zinc oxide 1.5, sulfur 1, accelerator 1 (wet, 1 day; dry, 1 to 3 days).

The statement above reads: "Wet, 1 day; Dry, 1 to 3 days." The wet period signifies the time of standing which elapsed between the preparation of the mix and the flowing of the sheets. The first figure of the dry period gives the period between flowing the sheets and vulcanizing them, and the second figure gives the time which elapsed between vulcanization and testing.

Ammonia-preserved centrifuge concentrated latex of 60 per cent dry rubber content was used throughout the series of experiments to be described in this paper, with the exception of one series of tests concerned with vulcanized latex. It is therefore proposed, in order to avoid repetition, to refer to this material as latex.

The following procedure was adopted as standard practice in the case of all heat-cured latex films. After standing for 24 hours to remove air bubbles, the mix was submitted to 10 minutes' slow mechanical stirring and was then flowed onto glass plates, dried, and vulcanized in the manner already described. In all the work to be described in this paper, sulfur and zinc oxide were added separately to the mixes in

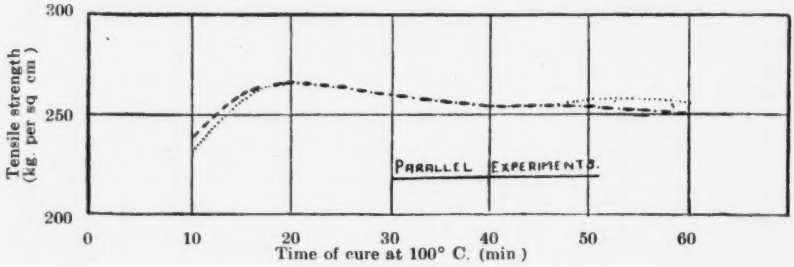


Figure 8

the form of 50 per cent aqueous dispersions. These were prepared as follows: In the case of sulfur, a paste consisting of sulfur 50, fluid proprietary dispersing agent 6, and water 44, was ground for two days in a gravel mill, that is, a ball mill charged with a mixture of 0.75 inch diameter porcelain balls with five times their weight of gravel passing a 0.25 inch sieve. In the case of zinc oxide, a ball mill was used, the paste being ground for 24 hours and consisting of zinc oxide 50, fluid proprietary dispersing agent 3, and water 47.

Mixes were always submitted to mechanical stirring immediately before flowing took place. The apparatus used was designed to avoid all tendency to draw air into the latex, and consisted essentially of two glass rods, each 0.25 inch diameter and mounted so as to lie 1.5 inches apart parallel to and on opposite sides of an imaginary projection of the axis of the stirrer. The stirrer rotated at a speed of 50 revolutions per minute.

Figure 8 is a typical illustration of the ability of this water-bursting technic to furnish consistent reproducible results. The above latex mix was compounded and then divided into two portions, which were subsequently handled as separate mixes, of which the vulcanization speeds were to be compared by means of tensile strength determinations under identical conditions. Sheets were flowed 7 days after the preparation of the mix, allowed to stand 1 day, vulcanized, and tested after 2 days. It will be seen that within closer limits of error than those tolerated nor-

mally in tensile testing, the graphs may be said to coincide. They show considerable activation of cure, due to a long period between compounding and flowing the sheets.

In operating the water-bursting test, it had from the beginning been the practice to use a valve on the water mains which, when opened fully and allowed to run freely, would pass about 1400 cc. of water per minute. In bursting a disc, the valve was always open fully, and with the actual pressure on the mains this took from about 15 to 20 seconds to inflate and burst the disc. Some enquiry was however made into the effect of varying the rate of water flow with the result shown on the accompanying graph (Fig. 9). The ordinate shows the values for bursting pressure divided by the thickness of the discs, and the abscissa measures the rate of inflation of the discs in terms of the volume of water passed per minute by the valve setting used without any discs in the die. The test-discs used were cut from (100° C.) cured sheets prepared from the usual mix, two curves being plotted for under-cured (5 minutes) and fully cured (30 minutes) samples, respectively. It will be observed that over a certain range of rates of inflation the recorded values of bursting pres-

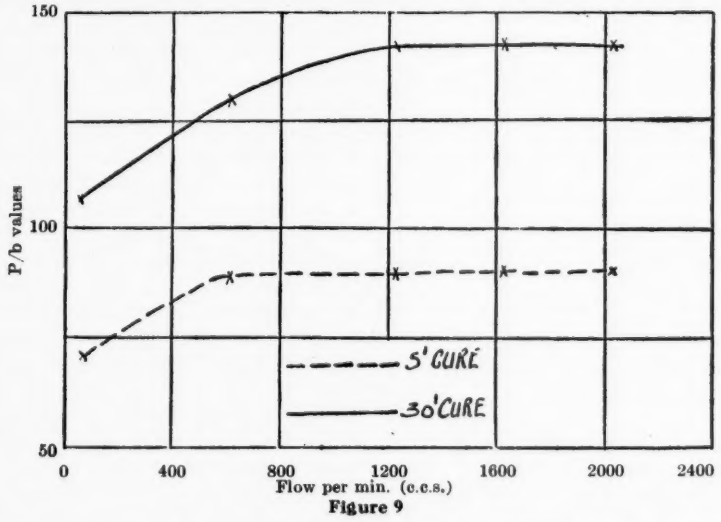


Figure 9

sure divided by the thickness of the discs are constant. The authors attribute the importance of using a rapid rate of inflation to the effect of water in weakening the bubbles if there is sufficient time for it to soak into the latex rubber. It is observed that if bubbles are held at degrees of inflation much inferior to the normal volume at bursting, they burst spontaneously after periods of upwards of half a minute.

Means have been developed to permit the use of compressed air to inflate and burst the test-discs (see Fig. 10). In order to measure the value of V, the volume at burst, and hence arrive at the value of D, the apparatus shown in Fig. 10 was constructed and calibrated. It consisted essentially of a cylindrical metal container 12.5 inches high and 6 inches internal diameter standing upon the closed end, and having at the open top an accurately machined plane edge. A short metal pipe of 1 inch bore projected horizontally from the side near the base, and was joined to an elbow piece, into which was sealed vertically a piece of glass tubing of 2 inches bore and 2 feet in length. At the same time, the bursting die was bolted

to a flat lid of metal through which the pressure and the manometer leads passed with an air-tight seal. This lid was separate from the container. A bar of metal, hinged on a projection from the upper wall of the container, could be swung down into place to pass diametrically across the lid and engage in a hinged slot also attached to the wall of the container on the opposite side. A screw passing through the center of the bar was used to exert pressure upon the lid, squeezing it down on a soft rubber washer placed on the machined edge of the container.

For the calibration of this apparatus, the following method was employed. The lid was held in place to make an air-tight seal as described, the die hanging down inside the container and holding, in place of the test-disc, a thin but rigid disc of metal. Through a small hole in the lid plate there had been sealed the stem of a tap funnel, to which was attached, on the inner side of the plate, a stout toy balloon of latex rubber. Both the balloon and the stem of the funnel were filled with water, all air being carefully excluded; the balloon was then pressed flat and the cock of the tap funnel closed. At the beginning of the calibration, a quantity of water was placed in the container, so that the water level just appeared in the lower part of the glass tube. Air was now forced through an extra tap in the lid so that the water level rose to a height of about 12 inches on the wide glass tube. In this condition, the apparatus was allowed to stand to verify the absence of all leakage of air and the water level was then returned to normal. Known volumes of water were now forced by pressure through the tap funnel into the balloon, and for each addition to the balloon the corresponding water level in the wide glass tube was marked and labelled with the total water content of the balloon. In this manner, a purely empirical calibration of the glass tube was effected, so that, starting with the water level of the system at zero of the scale, any decrease in the volume of the sealed space within the cylinder (due, for example, to the inflation of a test-disc on the die) could be read directly in cubic centimeters from the position of the water level on the scale of the water manometer tube.

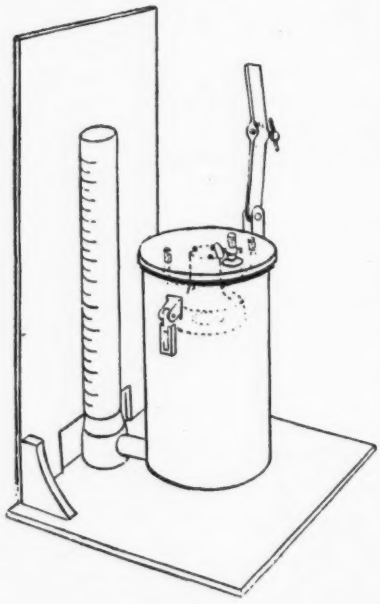


Figure 10

The procedure in taking a reading was as follows: After fitting the disc to the die, sealing the system, and testing for air leaks, the disc was inflated by means of compressed air. The observer followed the slow rise of the water level in the glass tube and recorded the scale reading at which burst occurred. At this point the water jumps nearly to the top of the tube through the sudden release of the pressure.

Evidently there are certain objections to this method. Thus the apparatus is more costly than that required for the water-burst method, and the tests take longer, since the system must be sealed and tested for each determination. The use

of air pressure is itself objectionable, owing to the high compressibility of air and the consequently large energy released when any part of the system breaks down. This makes difficult the use of any but a visual method for measuring the volume of the bubble at a break, and would render dangerous the accidental failure of any other portion of the apparatus. Compressed air is by no means generally available in a laboratory, and our aim was to develop a test which could be available in the absence of all machinery.

On the other hand, the air-bursting method shows over the water method the advantage of being less liable to slipping of the test-disc when careful attention is not given to the precautions already indicated, namely, having the rubber facings on the washer perfectly smooth and plane, drying them thoroughly, and wiping with benzene before placing the test-disc in position. A more important point is that the air-burst method makes possible the determination of a series of stress-strain values on the same sample. If the rubber and water are in contact for more than a few seconds, the rubber absorbs the water and is thereby weakened. Consequently, the bubbles must be inflated rapidly, and if inflation is stopped short of the bursting point for a pressure and volume reading to be taken, *i. e.*, for a modulus determination, any further tests will give low values. It is difficult to make a number of observations while inflation is proceeding at the proper rate, owing to the considerable lag between the actual volume of the bubble and the volume of displaced water in the cylinder. The air-burst method permits the bubbles to be held for a reasonable time at a given volume without weakening, and further is not subject to any appreciable lag between the volume of the bubble and the volume registered by the water manometer.

Neverthelesss, the authors are not at present prepared to present evidence in support of the use of the air-burst technic for routine physical testing of latex rubber.

Derivation of the Formulas

At the outset, it appeared that by far the simplest case to treat mathematically would be the case of a spherical bubble; any less simple shape would involve a knowledge of the ratios of linear dimensions. Further, approximations which would simplify matters would be to assume that the bubble is an uninterrupted sphere, *i. e.*, to neglect the break in its surface formed by the aperture of the die and the means whereby the fluid pressure gains access to the sphere, and that the entire mass of rubber contained in the free portion of the test-disc is formed into a shell of uniform thickness of which the bubble is composed.

The next step was to establish a formula on these simplified lines in order that practical data could be obtained which, it was hoped, might justify the approximations proposed. This was achieved in the following manner. It was first necessary to find an expression for the tensile strength referred to the final cross section of the test-piece. In the strip test-piece under uni-dimensional stretch, this is simply the total load on the breaking strip, in units of weight, divided by the area of the cross section normal to the line of pull. In the case of a hollow sphere of thin but uniform wall thickness, an equatorial section is considered. This section exposes a circular strip of rubber around the circumference of a great circle, which strip was taken as the equivalent of the rectangular section normal to the line of pull considered in a strip test-piece. The total stretching load on this circular section of rubber (expressed as the component of the force normal to its surface in units of weight per unit area multiplied by the area of the rubber section) must be in equilibrium with the component, normal to the equatorial section, of the fluid

pressure acting on the inner surface of either hemisphere and this component is equal to the fluid pressure within the sphere (expressed as units of weight per unit area) multiplied by the total area of the equatorial section of the sphere. At the moment of break, the component of the stretching load normal to unit area of this circular section of rubber was taken as the tensile strength of the rubber referred to the final cross section. In other words,

when T' = tensile strength on the final cross section of the rubber.
t = thickness of the rubber film at burst.
r = radius of the spherical bubble at burst.
P = fluid pressure within the bubble at moment of burst.

then $$r^2P = 2\pi rtT'.$$

Thus $$T' = \frac{rP}{2t} \qquad (1)$$

Now the surface area of the sphere is $4\pi r^2$, while the surface area of that portion of the test-disc which is free to expand is πa^2, a being the radius of this free area.

Thus a given unit of area on the original disc becomes $\frac{4\pi r^2}{\pi a^2} = \frac{4r^2}{a^2}$ units on the inflated bubble.

Consequently a given unit of length on the original disc becomes $\sqrt{\frac{4r^2}{a^2}}$ which is $\frac{2r}{a}$ on the inflated bubble.

It may be noted that E_B (the elongation at break) $= \frac{2r}{a}$.

By definition of the symbols, unit thickness in the final film was $\frac{b}{t}$ units on the original disc. A unit length on the final film would have been $\frac{a}{2r}$ on the original disc. It follows that a unit of cross-sectional area on the final film would have been $\frac{ab}{2rt}$ on the original film.

Thus, if T is the tensile strength referred to the original cross section,

$$T = T' \times \frac{2rt}{ab}.$$

So, from (1),

$$T = \frac{rP}{2t} \times \frac{2rt}{ab} = \frac{r^2P}{ab}.$$

From the practical point of view this formula appeared satisfactory, as the observations required for its application were all of a type which could accurately and rapidly be made with simple apparatus. On the other hand, the derivation of the formula had been based on assumptions which were obviously unjustified, and therefore could not stand without confirmation.

On reflection it was clear that a pure gum stock disc would not be in the shape of a sphere at the moment of bursting. It might pass through an intermediate phase during which it was a truncated sphere, but obviously from consideration of

the shape of the rubber stress-strain curve it would be a flattened spheroid before bursting. A metal disc, on the other hand, with its entirely different stress-strain curve, could pass from the sphere to the vertically elongated spheroid before bursting.

Furthermore, an aperture of 2.54 cm. diameter in a bubble about 10 cm. in diameter is by no means negligible; it could be seen that the bubble was not spherical but a flattened spheroid; and apart altogether from considerations on the mechanism whereby a disc of rubber assumes the spheroidal form, it was shown by a study of the final positions of a measured system of dots made on the uninflated disc that substantially less than half the rubber in the free portion of the disc was situated above the equatorial plane of the bubble. The rubber could therefore not be considered as being distributed as a sphere of uniform thickness. At this juncture another formula was derived.

When P = fluid pressure within the bubble.
r = radius of bubble at the equator.
a_e = the radius, on the original disc of rubber, of the circle which finally becomes the equator of the bubble.
b = original thickness of the disc,
the total load F on the inflated rubber at the equator equals $P\pi r_e^2$. Now, the equatorial cross section had originally a cross section of $\pi 2a_e b$. Thus, the load F referred as a tension T to the original cross section gives $\mathrm{T} = \dfrac{Pr_e^2}{2a_e b}$.

If the symbols represent the conditions at the instant of burst, T might be taken as the tensile strength of the rubber of which the disc is composed.

This formula appeared to introduce experimental difficulties absent from the first formula. Thus, a_e has to be known or determined, and r must be measured as a linear dimension at the moment of observation, as recognition of the nonspherical form of the bubble forbids calculation of r_e from the volume until practical justification has been furnished for this step. These practical difficulties, at the worst, could only prevent the use of the formula, and do not invalidate its theoretical value. On the other hand, observations of the behavior of inflated discs when near to the point of rupture and when actually burst showed that certain errors were still inherent in the formula itself. The petal structure of the burst discs suggests that the bubbles burst at the pole. Actual measurements of the thickness of the inflated films when near the point of burst, made by measuring the size on the bubble of spots of known dimensions made on the disc before inflation, show that the bubbles actually are thinner at the pole than at the equator. Hence the tension on the rubber must be greater at the pole than at the equator where it is measured by the formula.

In an endeavor to allow for these errors, a section of the spheroid may be considered as cut through a circle of longitude instead of through the equator. Thus, the stresses in the rubber perpendicular to this section will be those acting along the circles of latitude. These are the stresses responsible for the variation in thickness of the film between the equator and the pole. That the stresses acting along the lines of longitude are not responsible for these variations is evident from the fact that the bubbles are symmetrical about the polar axis, and that any section along a circle of latitude shows a section of rubber of uniform thickness. The stresses along the lines of latitude are thus those which cause the variation in film thickness. Further, the petal structure of the burst film indicates that the latitudinal stresses are those which actually cause rupture. These stresses must be measured in units

of force per unit of length, as in the case of surface tension forces generally. Thus, it may be stated that surface tension forces acting along the lines of longitude are constant for all parts of the bubble, but that surface tension forces acting along the lines of latitude vary, in the upper half of the spheroid being least at the equator and greatest at the pole. At the pole, the longitudinal and latitudinal surface tension values become equal. Hence, it may be said that the surface tension at the pole, which is responsible for bursting the film, is equal to the longitudinal surface tension at the equator. This last is evidently $\frac{Pr_e^2\pi}{2r_e\pi}$ or $\frac{Pr_e}{2}$.

As a matter of convention in measuring rubber tensiles, the breaking stress must be referred to the original cross section at the pole. If rubber be assumed to be

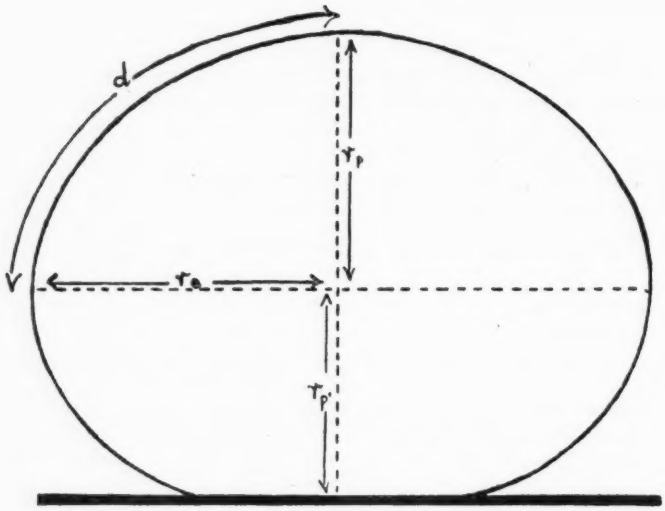


Figure 11

effectively incompressible, a line of final length l is related to its original length l_o by $l^2t_p = l_0^2b$ where b is the original thickness of the uninflated rubber.

When l is one unit, $l_o = \sqrt{\frac{tp}{b}}$, and the original cross section is $b\sqrt{\frac{tp}{b}}$.

Thus, when T is the tension on the rubber at the pole of the bubble (expressed in units of force per unit of original cross section).

$$T = \frac{Pr_e}{2\sqrt{t_pb}}.$$

This formula relates to the point of the bubble at which rupture begins, so that if the values for P, r_e, and t_p are observed at the moment of burst, T is the tensile strength of the rubber.

A formula, which is thus independent of any artificial assumptions, must be compared with the original formula which was based on a number of assumptions. The original formula is

$$T = \frac{Pr^2}{ab}.$$

As a is fixed for a given piece of apparatus and b is measured before the experiment is made, the observations which have to be made to determine T at a given degree of inflation are P the pressure and V the volume of the bubble. Even at the moment of burst both P and V are easily determined. In the true formula, to determine T for a given degree of inflation one must measure P, r_e, and t_p. The linear dimension r_e is obviously more difficult to measure than V even when T is to be determined at some state other than the moment of burst. To measure t_p with sufficient accuracy is a still more difficult matter. The method of measuring the size of spots or lines is subject to the difficulty of making an original mark of sufficient density to be clearly visible when highly distended without affecting the properties of the rubber. Could this difficulty be overcome, the measurements would have to be made by means of a telescope or by photography, either method needing rather an elaborate technic.

It was therefore sought to eliminate t_p from the expression. It has been seen that at the pole the equatorial and longitudinal surface tensions are equal. The latter is a constant for any point on the bubble, but the former decreases as one travels from the pole to the equator. Imagine the upper hemisphere to be isolated, and let conditions be such that the latitudinal surface tension does not decrease. The thickness at the pole of the bubble is not affected, but the thickness of the rubber is everywhere else reduced to the polar thickness. Distances from the pole to the equatorial circle do not vary, because the tension in this direction remains constant, but the distances between the lines of longitude are opened up until the hemisphere becomes a flat disc of rubber of uniform thickness. This thickness $t = \frac{ba_e^2}{d^2}$, b being the original thickness of the uninflated rubber, a_e being the radius on the original disc of the circle which finally becomes the equator of the bubble and d being the radius of the final disc. But it has been seen that $t = t_p$, the polar thickness of the final hemisphere, and as the imaginary treatment of this hemisphere would not affect longitudinal distances, d equals the shortest distance, measured on the surface of the hemisphere, from the pole (Fig. 11) to the equator.

Therefore $t_p = \frac{ba_e^2}{d^2}$, and substituted in $T = \frac{Pr_e}{2\sqrt{t_p b}}$, gives $T = 2\frac{Pr_e}{\sqrt{\frac{b^2a_e^2}{d^2}}}$ or $\frac{Pr_e d}{2a_e b}$. It should also be noted that E_B, the elongation at break, may be written $\frac{d}{a_e}$ instead of $\frac{2r}{a}$.

The mathematical comparison of this final formula with the original formula is of interest. They are, respectively,

$$T = \frac{Pr^2}{ab} \text{ and } T = \frac{Pr_e d}{2a_e b}.$$

Let $$\frac{Pr^2}{ab} \times f = \frac{Pr_e d}{2a_e b}, \text{ where } f \text{ is a factor.}$$

Then $$= \frac{dr_e a}{2r^2 a_e}.$$

Now $r = \sqrt[3]{\frac{3v}{4\pi}}$, v being the volume of the bubble, and this equals $\sqrt[3]{r_e^2 r_p}$.

Let $r_p = r_e(1 - x)$, x being a quantity which is small in comparison with unity. Then $r^2 = r_e^2(1 - x)^{2/3}$.

This, neglecting insignificant terms, is $r_e^2\left(1 - \frac{2}{3}x\right)$.

Now $$d = \frac{\pi}{4}(r_e + r_p) = \frac{\pi}{4} r_e(2 - x).$$

Therefore,

$$f = \frac{\frac{\pi}{4} r_e^2 a(2 - x)}{2r_e^2 a_e\left(1 - \frac{2}{3}x\right)} = \frac{\pi}{8} \cdot \frac{a}{a_e}\left(2 + \frac{x}{3}\right) = \frac{\pi}{4} \cdot \frac{a}{a_e}\left(1 + \frac{x}{6}\right).$$

Now x being by definition small compared with unity, $\frac{x}{6}$ would for practical purposes be negligible.

Thus, $f = \frac{\pi}{4} \cdot \frac{a}{a_e}$ and values of T obtained by the first formula and its experimental technic could be converted into the true values of T by multiplication by $\frac{\pi}{4} \cdot \frac{a}{a_e}$.

It is to be noted that a being fixed by the apparatus in use, a_e is the only possible variable.

Experimental Investigation of Formula Approximations

It remained to devise a method of determining a_e at any given degree of inflation and especially at the moment of burst, in order that the values might be used to determine the magnitude and variability of the correction factor. With ink and a fine mapping pen, a tiny center spot was marked on the test-disc of rubber and then along an imaginary radius and after a convenient interval, a series of tiny dots was made, each about 0.5 mm. apart. By means of a fine steel scale and a lens, the distance of each dot from the center spot was measured. The disc was accurately centered and clamped in the bursting die and then inflated to the size of a plum. At this degree of inflation the distended spots, which underwent a corresponding reduction in visibility, could just be distinguished. By means of a fine brush dipped in ink, the center of each distended dot was plainly marked with a fresh dot, and to assist observation, a fine line was drawn half-way between each dot. In practice, once the limits of the a_e values had been observed, it was only necessary to make a few dots on the disc, starting at about 6 mm. from the center, so that the whole operation (including the re-inking) was quickly done. Inflation was then continued rapidly until the disc burst. No difficulty was experienced in observing and estimating the position on this marked scale of the equator, even at the instant of burst. Determinations were made, inflating with either air or water. In the latter case, the discs were partially inflated with water, re-inked with a quick-drying ink (*e. g.*, a solution of Victoria Blue in benzene), and re-immersed in the water-displacement can for inflation to the desired volume, or to the point of rupture. Observations were made through a glass window in the side of the container (Fig. 12).

It was found of interest actually to make some determinations of r_e and d as well as a_e at degrees of water inflation near the bursting point. This was done by photographing the marked bubble through the glass window, placing the camera in the equatorial plane and at a suitable distance. The scale of the photograph was given by the known width of the bursting die itself. Thus, a_e, r_e, and r_p could be measured on the plate and as

$$d = \frac{\pi}{4}(r_e + r_p)$$

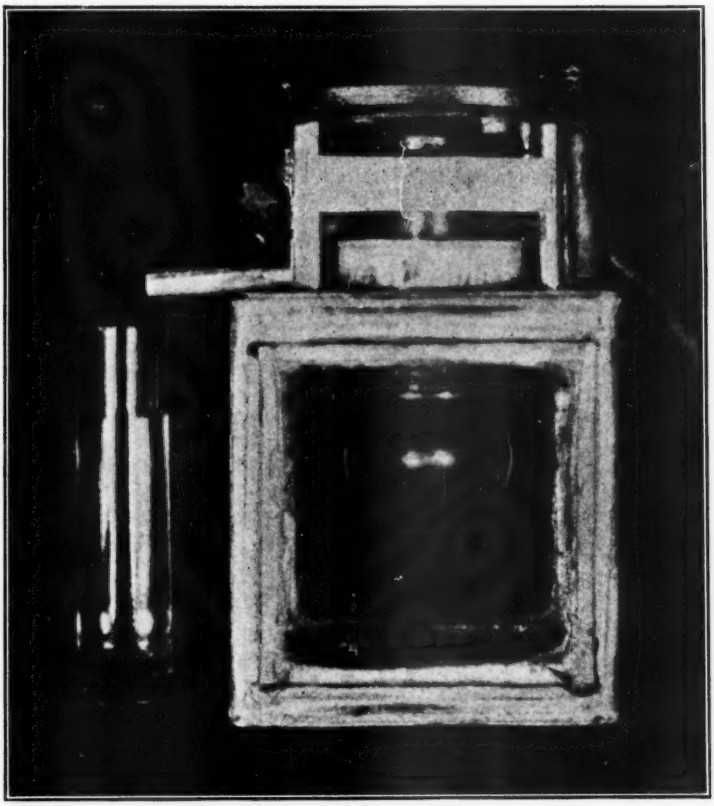


Figure 12

the value of d could be calculated. The volume of the bubble at the moment of observation was read from the volume of water displaced. Had these values been required at the instant of burst, a cinema film could have been taken, the measurements being made on the last exposure before bursting occurred. It was not, however, proposed actually to determine the tensile strength of rubber samples by this technic. The intention was to use it for further confirmation of the original formula and technic. The method adopted was as follows. Eliminating $\frac{P}{b}$

from the two formulas, it was required to show the relationship of $\frac{r^2}{a}$ to $\frac{r_e d}{2a_e}$ and then to compare this correction factor with $\frac{\pi a}{4a_e}$, to which it should be equal within the limits of error tolerable in this work.

It has been observed that the a_e value increases with the degree of inflation. Thus, if a line be painted around the equator of a bubble at a relatively low degree of inflation, the line is seen to move up towards the pole as inflation continues.

From examination of many a_e values, determined at the point of burst, it appeared that this value is independent of the thickness of the test-disc within the limits of variation handled, and is a constant for a given sample of rubber. Actual values determined on the vulcanized sheets having the stated composition are as follows:

Description of Rubber and Accelerator Used	Average a_e Value in Mm. (a Is 12.7 Mm.)
1. Uncompounded, unvulcanized	7.1
2. Vulcanized 5 minutes at 100° C. with diethylammonium diethyldithiocarbamate	7.1
3. Vulcanized 30 minutes at 100° C. with diethylammonium diethyldithiocarbamate	7.4
4. Vulcanized 30 minutes at 100° C. with piperidine pentamethylenedithiocarbamate	7.4
5. Vulcanized 30 minutes at 100° C. with zinc diethyldithiocarbamate	7.7
6. Vulcanized 60 minutes at 120° C. with butyraldehydeaniline	7.7

It will be seen that an unvulcanized rubber (1) and an under-vulcanized rubber (2) give identical results, the lowest observed. Next in order of magnitude are those furnished by full, but fairly low modulus cures (3) and (4). Finally the highest results are given by the two high modulus cures (5) and (6). The observed range of variation is between 7.1 and 7.7 mm. for the standard die opening which is 12.7 mm.

It has already been shown that results obtained by the original formula and technic should be multiplied by a factor for which $\frac{\pi a}{4a_e}$ might, in practice, be a sufficiently accurate approximation, assuming the factor $\left(1 + \frac{r_e}{6}\right)$ close to unity. It now appears that, at any rate for the normal types of latex rubber, the range of variation of a_e is from 7.1 to 7.7 mm. and that the full range of variations may be found in a series of cures from the same compound. Thus, $\frac{\pi a}{4a_e}$ might vary from 1.29 to 1.40, and if the mean value 1.35 were employed as a correction factor, the results would only be subject to an error of ± 4 per cent.

The technic already described in which a disc, marked with a line of dots each of known distance from the center, is inflated with water in water and then photographed, has been found thoroughly practicable. This method was adopted to determine (1) the magnitude of x and thus whether the factor $1 + \frac{x}{6}$ could for practical purposes be neglected; (2) whether the bubble was a true spheroid, *i. e.*, whether it was symmetrical about the equatorial plane. On (2) depends the accuracy of

the expression $r = \sqrt[3]{r_e^2 r_p}$ used in deriving the extra factor $\left(1 + \frac{x}{6}\right)$ and hence the validity of that factor.

Up to the time of writing, only a few determinations have been made, the films being of uncured latex rubber or of latex rubber of the formula just given, fully vulcanized with diethylammonium diethyldithiocarbamate. They were photographed when inflated almost to the bursting point.

It was at once seen from the plates that the bubbles were quite definitely not symmetrical about the equatorial plane. The lower polar radius was noticeably smaller than the upper polar radius. This, it should be noted, in no way affects the validity of the formula $T = \frac{r_e dP}{2a_e b}$ but only the way in which this is related to $T = \frac{r^2 P}{ab}$. Further, the whole bubble was, at the bursting point, a very obviously flattened spheroid. The true correction factor is, evidently, $\frac{r_e dP}{2a_e b} \times \frac{ab}{r^2 P}$ which is $\frac{r_e da}{2a_e r^2}$.

This requires so many observations that it would be simpler and more accurate to use the final formula itself.

There is $\frac{\pi a}{4a_e} \times \left(1 + \frac{x}{6}\right)$ as a first approximation, which involves a knowledge of x and would only be of practical value if x had an approximately constant value or if the factor $\left(1 + \frac{x}{6}\right)$ were almost unity. As already noted, a_e may be predicted with sufficient accuracy or if greater precision is required, may easily be determined by visual observation at the moment of burst.

In the cases investigated, x varied from 0.14 to 0.16 for cured and uncured rubbers, respectively, the factor $\left(1 + \frac{x}{6}\right)$ thus varying from 1.023 to 1.027.

This factor is small enough to neglect and, in any case, seems to be sufficiently constant for its use to be without effect on the relative accuracy of the figures. It remained to see whether the lack of symmetry in the bubble would introduce an error of sufficient magnitude to render $\frac{\pi a}{4a_e} \times \left(1 + \frac{x}{6}\right)$ ineffective as a correction factor.

In most cases investigated $\frac{r_e da}{2a_e r^2}$ gave true correction factors of 1.30 and 1.46, respectively, for the cured and unvulcanized latex rubber. The corresponding values of $\frac{\pi a}{4a_e} \times \left(1 + \frac{x}{6}\right)$ were 1.22 and 1.40, and of $\frac{\pi a}{4a_e}$ alone were 1.19 and 1.37.

The effect of the lack of symmetry can thus be clearly seen. With $\frac{\pi a}{4a_e}$ as the correction factor, the gross errors involved are 8.5 per cent for the fully vulcanized rubber and 6.2 per cent for the unvulcanized rubber. Measurement of the photographs showed lack of symmetry to be more pronounced in the vulcanized than in the unvulcanized bubbles. The errors, when introduced by the use of a correction factor, are too great from the point of view of absolute accuracy; but if the average

value of 7.3 were used, or if one considered only the effect of these limits on the relative accuracy of tensile figures computed from $\frac{r^2P}{ab}$, the error is only ± 1.15 per cent.

The observed variations in a_e introduce an error into the relative accuracy of the original formula of about ± 4 per cent. Adding this further source of error due to variations in the degree of asymmetry of the bubbles brings the error up to about ± 5 per cent.

It may thus be concluded that, within the limits of error which may be tolerated in the physical testing of rubber, the original formula gives results which differ only from the true tensile strength values by a constant. Hence, as only relative results and not absolute figures are required for normal work, *e. g.*, note the consis-

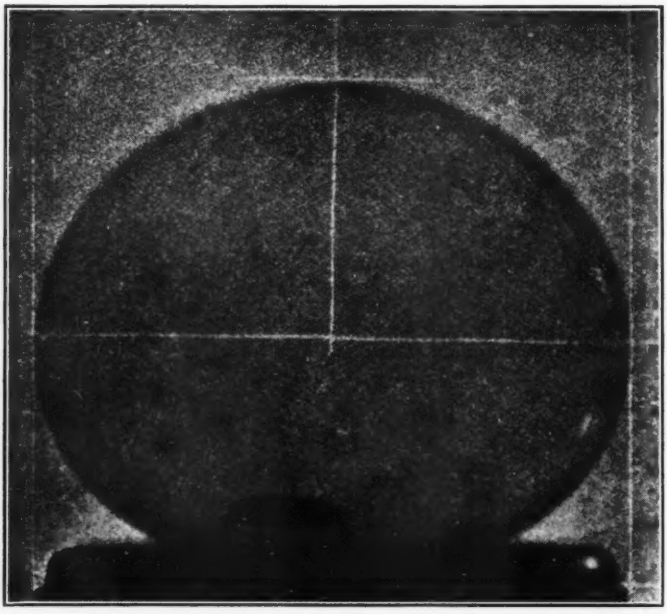


Figure 13

tent differences between results furnished by ring and dumb-bell test-pieces, the figures from the original formula may in practice be accepted without change. It should be noted that, on Figs. 7, 8, 14, 15, 16, 17, 18, and 19, the tensile figures have been calculated using the original uncorrected formula, and are therefore about 25 per cent too low.

It is of interest to calculate the actual polar thickness (t_p) of the bubbles at the moment of bursting.

Now $t_p = \frac{ba_e^2}{d^2}$, but $d = \frac{\pi}{4}(r_e + r_p) = \frac{\pi}{4} r_e(2 - x) = \frac{\pi r_e}{2}\left(1 - \frac{x}{2}\right)$.

Neglecting $\frac{x}{2}$ and substituting for d gives $t_p = \frac{4ba_e^2}{\pi^2 r_e^2}$. Normal values in practice are $b = 0.4$ mm., $a_e = 7.4$ mm., $r_e = 45.0$ mm.

These give $t_p = 4.5\mu$ as the order of thickness encountered in practice. t_e, the equatorial thickness, may be calculated from $t_e = \frac{t_p d}{r_e}$. This may be written $t_e = \frac{t_p \pi r_e}{r_e 2}\left(1 - \frac{x}{2}\right)$. This, taking x as 0.14, gives $t_e = 1.44\, t_p$.

Actual determinations of t_p and t_e values, made by making ink spots of known size on the discs and measuring the size of the spots when the bubble was inflated almost to the bursting point gave values of the same order of magnitude as those just quoted.

The relative dimensions of the bubble practically at bursting point may be seen from the photograph (Fig. 13).

Actual measurements for an uncured bubble were $r_e = 45.7$ mm.; $r_p = 38.0$ mm.; $r_{p'} = 34.2$ mm. and for a fully cured bubble $r_e = 45.3$ mm.; $r_p = 39.3$ mm.; $r_p = 33.3$ mm.

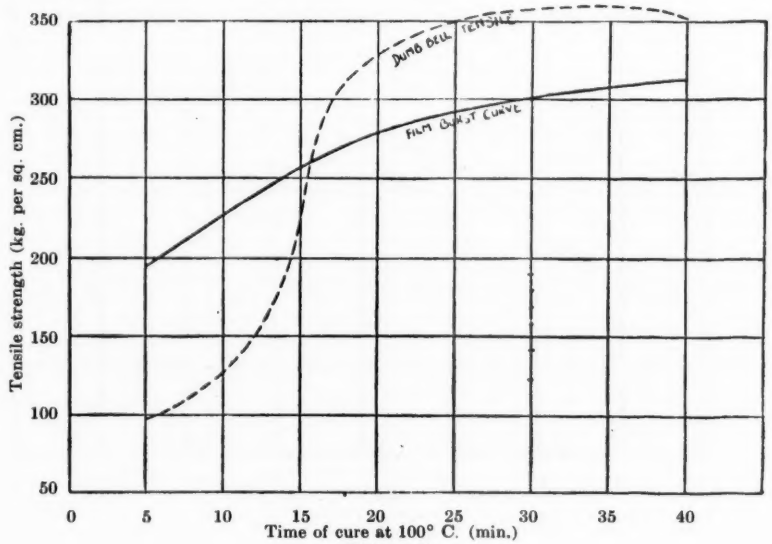


Figure 14

The symbol $r_{p'}$ represents the lower polar radius.

It is now possible to compare the original and final formulas for the elongation of the rubber (which gives the elongation at break if used at the bursting point of the bubble). They are respectively $\frac{2r}{a}$ and $\frac{d}{a_e}$. The correction factor for the first formula is $\frac{da}{2ra_e}$. This reduces to $\frac{a}{a_e} \cdot \frac{\pi}{8} \cdot \left(2 - \frac{x}{3}\right)$. Substituting $a_e = 7.4$ and $x = 0.15$, this has a value of about 1.30. Thus it would appear that elongation figures calculated by the original formula should be multiplied by a factor whose value is, for practical purposes, 1.30 to give the true values.

It should be pointed out that the value of a photographic method in working with the new formula lies in the difficulty otherwise of determining d. This is calculated from the value r_p, which is the vertical distance from the top of the bubble to its

point of greatest width. The rounded curves of the bubble make it difficult to fix this point of greatest width with adequate accuracy by any purely visual observation, either at the instant of burst or in the short time available at any other degree of inflation. The greatest width of the bubble can be measured with accuracy; the difficulty is in measuring accurately the distance of the equator from the pole. A photograph allows the use of geometrical devices to fix the required point.

The height or width of a bubble may be measured easily and accurately at any moment, including the instant of burst, by relying on the fact that the bubbles are very firm and are not distorted by a light contact. The measurements are made by pieces of steel rod mounted to slide smoothly and easily in horizontal bearings. Each rod ends in a buffer disc about half-inch in diameter, and a mark on the rod can be read against an accurately graduated linear scale. The die is mounted

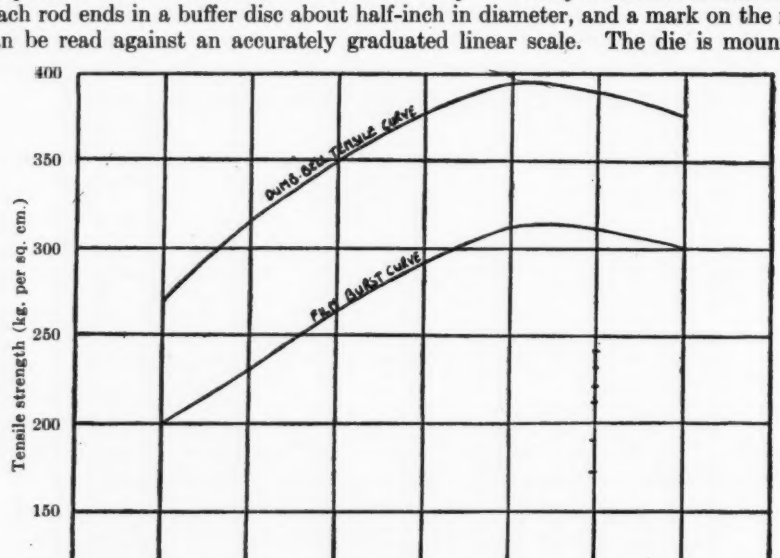


Figure 15

horizontally, and a pair of the measuring rods are placed to lie in the same horizontal plane as the axis of the die. One rod is aligned with this axis and the other is at right angles to it. As the bubble is inflated, it presses against the disc heads of the rods, moving them without suffering any distortion, thus enabling the equatorial radius and the polar diameter of the bubble to be read directly from the scales. It is observed that the bursting of the bubble leaves the measuring rods as they were the instant before burst occurred.

It may be noted that the formula,

$$T = \frac{r_e dP}{2a_e b},$$

on substituting $d = \frac{\pi r_e}{2}\left(1 - \frac{x}{2}\right)$ becomes

$$T = \frac{\pi r_e^2 P}{4a_e b}\left(1 - \frac{x}{2}\right).$$

In a series of fourteen determinations with latex films in various stages of vulcanization and cured with various accelerators $\left(1 - \frac{x}{2}\right)$ was found to have an average value of 0.926, no individual figure differing by more than ± 1 per cent from this average. The accelerators used were those for which a_e values have already been given, and zinc diethyldithiocarbamate.

The expression may thus be reduced to

$$T = \frac{0.73\, r_e^2 P}{a_e b}.$$

For each individual disc r_e might be determined at burst by the "sliding rod" method and a_e by the visual method already indicated. This formula is thus suggested as a means of determining the tensile strength by a simple air-bursting test which is entirely free from any inaccuracies introduced by the slipping or bulging of the rubber in the die.

Experimental Data Supporting the Proposed Method

It is now important to see how, in actual practice, the results furnished by this film-bursting test compare with those furnished by the standard physical testing technic. At first, no simple relationship could be observed between time tensile curves obtained by the two methods from the same series of cures. Every proper precaution was taken to ensure the uniformity of the sheets of latex rubber, and both dumb-bells and test-discs were cut, alternately spaced, from the same sheets. As a general rule, it was observed that the pulling-test curve started at a considerably lower tensile value than the film-burst curve, rose steeply to a substantially higher value, and then continued parallel to it. The point of intersection corresponded roughly to the point at which permanent-set falls to below about 7.5 per cent. A typical comparison is shown in Fig. 14, the latex rubber of stated composition having been cured with diethylammonium diethyldithiocarbamate.

A feature of the individual results furnished by the pulling test was the poor agreement among results obtained from a single cure, particularly during the early stages of vulcanization. This was attributed to edge imperfections in the thin test-pieces. At the higher stages of elongation on the tensile machine, these flaws could clearly be seen. A very sharp knife lubricated for each cut was being employed.

The superior quality of the test-pieces from the higher cures suggested that if the rubber could temporarily be hardened during the cutting process, satisfactory results would be received. It was accordingly resolved to try a freezing process.

A stout rectangular wooden trough was made of a size just sufficient to take a strip of latex sheet from which one dumb-bell could be cut. The trough was lined with tin plate, the seams being heavily soldered, and a thick pad of well-vulcanized rubber was laid inside to cover the bottom. A strip of the latex sheet was placed on the rubber pad, and the cutting knife was laid upon it, requiring only the application of pressure to cut the dumb-bell. The shank of the knife, well-lagged, was already beneath the cutting press. Methylated spirit was then poured in, covering the rubber to a depth of 1.5 inches, and carbon dioxide ice was added in small pieces until, on withdrawing a thin test-strip of rubber from the trough, it was found to be quite hard. Pressure was then applied to the knife.

No test-pieces cut by this method were tested until a lapse of 24 hours after

the freezing. It was at once apparent that the dumb-bells from even the low cures, or from unvulcanized latex rubber, were perfect, although the average thickness was in the neighborhood of 0.3 mm. Comparative tests against the film-bursting method now gave the two curves running practically parallel, the lower curve being that for the film-bursting method. Actually, the lower tensile figures were slightly nearer together than the higher figures, suggesting that multiplication of the lower curve values by a constant factor would give the higher curve. At the time of writing, this point has been verified only for the diethyldithiocarbamate accelerator, the latex rubber being compounded to the standard formula. A typical pair of curves is shown on Fig. 15.

It should be pointed out that the original formula, $T = \frac{r^2P}{ab}$, was used in calculating the film-burst values. For two of these pairs of comparative curves, the factors actually converting film-burst values to pulling test values were calculated. They were found to decrease from the neighborhood of 1.40 for the uncured rubber to 1.25 for the fully vulcanized rubber. It is of great interest to note how closely these factors correspond to the values of the correction factors for the film-burst formula calculated for the same type of rubber from $\frac{r_e da}{2a_e r^2}$. This formula gave 1.46 for the completely uncured rubber (1.40 from the comparison curves corresponded to a slight degree of heat cure) and 1.30 for rubber at a degree of cure for which the comparison curves indicated a factor of 1.28. Considering the formula $\frac{\pi}{4} \cdot \frac{a}{a_e}$, the range of factors 1.40 decreasing to 1.25 corresponds to the observed increase of a_e values as cure progresses and corresponds also to a_e values of the actual magnitude of those observed in practice.

There are thus good grounds for suggesting that the film-bursting test gives by the original formula tensile strength time curves which bear an approximately constant relation to the curves obtained by pulling dumb-bell pieces, and further that the film-bursting results obtained by the use of the true formula or the proper correction factor coincide with the dumb-bell tensile strengths.

As regards elongation at break, it is observed in practice that the original film-bursting formula of $\frac{2r}{a}$ also gives values which are substantially lower than those obtained from dumb-bells. When they are multiplied by a factor of the order of 1.30, which has already been derived from the final formula $\frac{d}{a_e}$, they give results of the order of those obtained from dumb-bells.

It is a matter of great interest that a method of bursting films by bi-dimensional stretch, *i. e.*, increasing their surface area, should give results in agreement with those obtained by unidimensional stretch, *i. e.*, pulling a dumb-bell. Not only do tensile figures coincide, but the elongation figures are of the same order. In other words, having stretched the rubber to the limit in one direction, it may be stretched to a similar extent in a direction at right angles to the first. An interesting and valuable discussion of this and related matters will be found in a paper by Sheppard and Clapson (*Ind. Eng. Chem.*, **24**, 782 (1932)). These authors have studied the stress-strain properties of rubber by inflating spherical balloons specially manufactured for their experiments.

It was now necessary to deal with a serious theoretical objection to the use of water. Although the disc is screwed up in contact with dried surfaces, and the

period between first contact with the water and the final burst is only a matter of about 15 to 20 seconds, it might be held that even under these conditions, water absorption might seriously weaken the film and thus lower its tensile strength. Careful comparison was therefore made (using a diethylammonium diethyldithiocarbamate—latex mix of the composition already indicated and curing the sheets at 100° C.) between the results obtained by use of the water-burst and air-burst methods, respectively. The principle of the comparison was that two sheets, instead of a single sheet, were submitted to cure for each of the selected periods, and three discs chosen at random from the six obtained from each sheet were tested by the water-burst method. The remaining three discs from each sheet were tested by the air-burst method, results obtained by each method being finally averaged after application of the selection rule already indicated. It will be seen from Fig. 16 that, within the limits of error to be anticipated in any tensile testing method, the two methods give fairly similar results. For the higher cures, the "water tensile strengths" are consistently higher than the "air tensile strengths."

Confirmation of these results indicated that for heat-cured films prepared from this latex, which is in effect latex in which the content of hygroscopic non-rubber

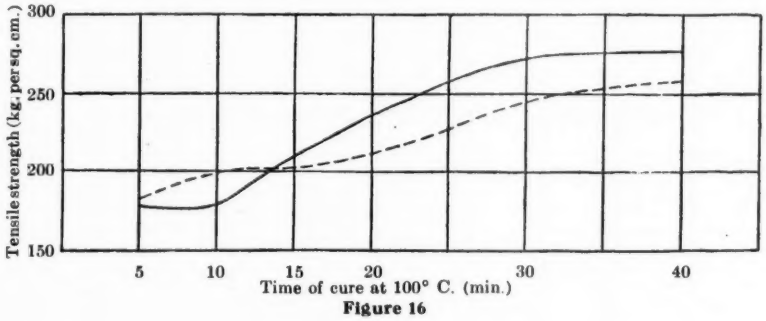


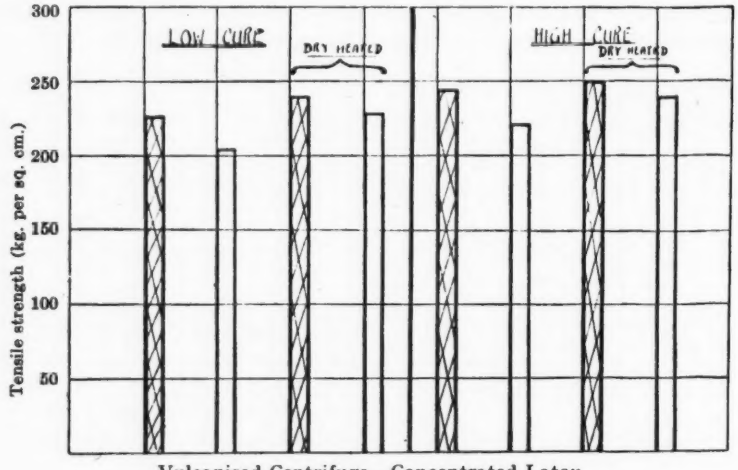
Figure 16

substances has been very considerably reduced, the mix being free from protective colloids other than the amount present in the sulfur and zinc oxide dispersion, the use of water for bursting the films is certainly free from adverse effects on the tensile figures secured.

It might, however, be further objected that air-dried films prepared from vulcanized latex might be more susceptible to the weakening effect of water. A centrifuged latex mix of the composition already employed was prepared in a similar way from similar materials, and was then divided into two portions, each container being immersed in a water bath which was maintained at 70° C. The beakers were covered by floating paper on the surface and were undisturbed during the heating and subsequent cooling. One sample was removed after 1.5 hours' heating and the second was removed after 2.5 hours; both were allowed to cool spontaneously to laboratory temperature. Finally, sheets were flowed and allowed to dry. The latex cured for 1.5 hours gave a film which still showed a considerable permanent set, whereas that cured for 2.5 hours dried to a film free from permanent set. Air-dried films both from the under-vulcanized and the fully vulcanized latex were tested by the water-bursting method and the air-bursting method (*a*) without further treatment, and (*b*) after treating the air-dried sheets for 10 minutes at 100° C. in the vulcanizing apparatus. The results are shown in Fig. 17, in which the tensile strength of the various samples is represented by the height of the columns.

It will be observed that, in each case, the tensile figure furnished by the water-burst method is slightly higher than that furnished by the air-burst. Dry heating the films puts up the tensile strength of the under-cured film, but has no effect on the rubber from the fully vulcanized latex; it also reduces the differences between the water-burst and air-burst results on the same sample. Thus, one is led to the conclusion that the water-burst method is suitable for use on air-dried films obtained from vulcanized latex prepared by vulcanizing this purified centrifuge-concentrated latex without addition of stabilizers other than the small quantities present in the sulfur and zinc oxide dispersions.

Attention was now given to the case of a vulcanized latex prepared from a heat-concentrated latex stabilized before the evaporation with non-volatile additions of fixed alkali and protective colloid. This latex, of 70 per cent rubber content and containing about 75 per cent of total solid, was compounded in the usual manner. In this case, the water bath was maintained at 80° C., and the compounded latex



Vulcanised Centrifuge—Concentrated Latex.

Water-burst Tests. ☐ Air-burst Tests.

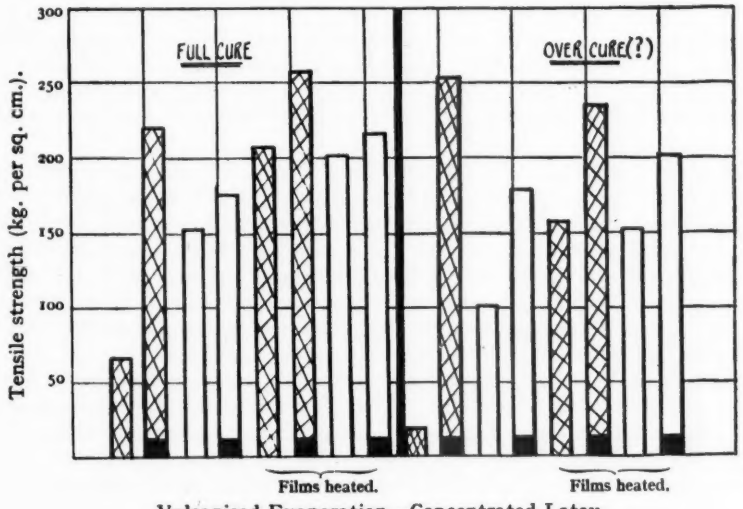
Figure 17

was vulcanized in two batches, which were kept in the bath for 1.5 hours and 2.5 hours, respectively, and then allowed to cool spontaneously before flowing took place.

This experiment differed from that already described in that vulcanization of the latex was effected at 80° C. instead of at 70° C. Thus 90 minutes' heating was certainly sufficient to ensure a full cure, and the period of 150 minutes would tend, if anything, to lead to over-cure. Otherwise the experiment was on similar lines to the last. Air-dried films of latex from each cure were tested by both water and air bursting, before and after 10 minutes' heating at 100° C. An additional factor was introduced by submitting samples of each of these four types of sheet to extraction with cold water for four hours, and then air-drying again. Results are shown in Fig. 18, in which the height of the column is a measure of the tensile strength of the sample as determined by either the water- or air-bursting technic.

In the case of the latex vulcanized for 1.5 hours at 80° C., it will be seen that the

"water" tensile figure of the untreated film is much lower than the "air" tensile figure, presumably by reason of the relatively large quantities of water-soluble stabilizers and other non-rubber substances present. Either cold-water extraction or dry heating, or dry heating followed by cold-water extraction will increase the



Vulcanised Evaporation—Concentrated Latex.

Water-burst Tests. ☐ Aireburst Tests.

■ Water-Extracted Samples.

Figure 18

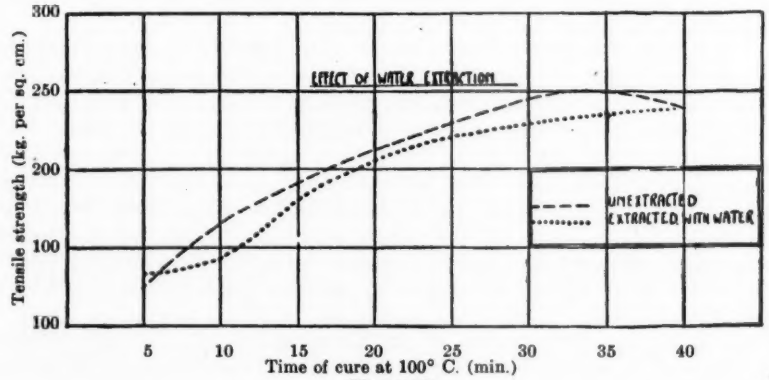


Figure 19

"air" tensile strength, the effect increasing in the order in which the factors have been named, and will eliminate the weakening effect of water on the film as shown by the water-burst figures. Where water extraction is used, the "water" tensile strength actually becomes definitely higher than the "air" tensile strength, as had

already been noted in the case of heat-cured films from compounded centrifuge concentrated latex, or air-dried films from vulcanized centrifuge concentrated latex. It is to be noted that the order in which these factors affect the water-burst tensile figures is somewhat different, *viz.*, dry heating, heating followed by extraction, and extraction.

With latex vulcanized for 2.5 hours at 80° C., it is seen that exactly the same considerations apply, save that cold-water extraction, dry heating, or heating followed by extraction increases the tensile strength of the air-dried film in different orders, *viz.*, in the increasing order of heating alone, extracting alone, and heating followed by extraction for the air bursts; and heat, heat followed by extraction, and extraction alone, for the water bursts.

In a comparison of the results obtained from the two batches of latex, vulcanized, respectively, for 1.5 and 2.5 hours at 80° C., it is evident that dry heating the films from the longer cure gives a weaker film in comparison with the shorter cure, the difference being least when the films are water-extracted. The untreated films, air-dried from the 1.5 hour batch and tested by air or water, are definitely stronger than those from the 2.5 hour batch, but water extraction of both types of film gives a result in favor of the longer cure, the difference being negligible in the case of the air tensiles, but quite definite in the case of the water tensiles.

It is thus evident that the water-burst technic is not applicable to air-dried films of a vulcanized latex containing a relatively high percentage of water-soluble non-rubber substances, but that even in so extreme a case, heat-cured films can be tested with satisfactory results. Other conclusions about the properties of such films are that in the case of a fully cured film, heat or extraction or preferably both are needed to develop good water resistance, and, in the case of over-cure, water extraction has a compensating effect in correcting any loss of strength.

As a matter of interest it may be remarked that, in the case of heat-cured films from the compounded centrifuged latex, desiccation of the fully cured films for 18 hours over calcium chloride had no effect on the tensile by the water-burst technic. The films were cured for 30 minutes at 100° C. Undesiccated samples showed an average tensile strength of 297 kilograms per square centimeter, and desiccated samples gave a figure of 298.

It will have been noted that the effect of water extraction on dry-heated films from heavily stabilized vulcanized latex, in the case both of the cured and somewhat over-cured sample, was to raise both the air-burst and water-burst tensile figures. This point was examined with respect to heat-cured films from the centrifuged latex.

Some of these films, after vulcanization, were extracted with cold water for 18 hours, and dried at air temperature before testing. From the results obtained by water bursting, curves were plotted for both the extracted and unextracted sheets (Fig. 19). It will be seen that in the case of latex relatively free from water-soluble stabilizers the observations already recorded are reversed; water extraction of heated sheets tends somewhat to lower the tensile strength as determined by film bursting.

Work is at present in progress covering the application of the above technic to the study of the curing of latex compounds both in the liquid and dried state and to the study of special latex accelerators.

In conclusion, the authors wish to express their thanks to A. B. D. Cassie and J. R. S. Waring for help in the mathematical treatment of the subject, and to Imperial Chemical Industries, Limited, for permission to publish the results embodied in this paper.

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Examination of Rubber Latex and Rubber Latex Compounds

I. Physical Testing Methods

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PRECISE control is essential to the successful operation of any commercial process, particularly of those processes involving the use of rubber latex. Latex is, of course, a complex natural product; it contains a variety of nonrubber constituents, such as proteins, soaps, and others which control or influence its colloidal properties. In order to ensure uniform behavior of latex in process, it is obviously desirable to test its uniformity as a raw product. It is furthermore important that such tests should be, wherever possible, fundamentally sound and free from the personal equation. Unless the results can be expressed in basic fundamental units, which are independent of the apparatus used and of the operator, confusion will result.

It is the purpose of this paper to review critically the more important general physical tests and methods of analysis which can be applied to latex, particularly from the standpoint of accuracy and sources of error, and to recommend certain procedures on the basis of commercial experience in the authors' control laboratories. Some of the recommended methods have been developed in these laboratories, while others have been improved over procedures given in earlier works on latex (*3*, *6*, *9*). Part I is concerned with physical tests such as pH, surface tension, viscosity, and mechanical stability, while Part II is concerned with analytical methods.

Sampling

It may appear superfluous to discuss methods of sampling latex, which are based on the same principles as sampling for any type of analysis. However, in view of the tendency of any type of latex to cream to a greater or less extent, it cannot be stressed too strongly that care should be taken to obtain a sample which is representative of the entire lot of material.

In the case of latex in drums, particularly concentrated latex, it is advisable to stir with a high-speed stirrer of the propeller type for a period of 10 to 15 minutes before taking the sample. In the case of tank-car lots, the latex

should be agitated with an air line which should be moved from one end of the car to the other, and agitation should be continued for at least one-half hour.

Measurement of pH

The pH of latex is probably one of its most important properties, inasmuch as it is related in a fundamental way to the stability of the latex as a colloid. However, only one of the methods which are generally employed for the measurement of pH is adapted to the accurate measurement of the pH of latex.

Indicators are unsatisfactory even for approximate measurements on account of protein errors and difficulties in matching colors. In view of the fact that the glass-electrode apparatus is commercially available, the use of indicators is to be avoided entirely.

The hydrogen electrode is also unsuited for use in latex, on account of the ease with which it is poisoned by certain sulfur-containing proteins and traces of hydrogen sulfide. Other difficulties are also encountered, such as frothing of the latex and a tendency for rubber to deposit on the electrode.

The quinhydrone electrode can, of course, be used only in solutions having pH values lower than 8, or below the pH region of most common practical interest in latex processing. For this reason its use in latex has not been extensively investigated in these laboratories. This electrode has, however, been used extensively by van Harpen (*5*) for measurements of the pH of natural latex.

TABLE I. COMPARATIVE PH VALUES

Samples	Total Solids, %	pH Determined by Glass Electrode *A*	pH Determined by Antimony Electrode *B*	Difference (*B* − *A*)
Normal latex				
A[a]	30	8.64	8.71	+0.08
B[a]	30	9.46	9.88	+0.42
C[a]	30	9.86	10.27	+0.41
D[a]	30	10.60	11.02	+0.42
E[a]	30	11.96	12.14	+0.18
F	30	9.57	10.11	+0.54
F	35	9.56	9.87	+0.31
G	37.9	9.89	10.26	+0.37
H	36.9	10.31	10.70	+0.39
I	39.3	9.62	10.03	+0.41
Concentrated latex				
A	30	9.46	9.58	+0.12
B	30	9.14	9.32	+0.18
C	30	9.32	9.56	+0.24
3-X creamed latex				
A	30	11.16	11.26	+0.10
B	30	10.60	10.51	−0.09

[a] Modified.

Before the glass electrode was manufactured commercially by Leeds & Northrup and other companies, considerable careful work was done on the calibration and use of the antimony electrode. While the potentials were sufficiently

reproducible in buffer solutions to indicate that an accuracy of 0.1 to 0.3 pH could be obtained (depending upon the pH of the solution), the accuracy was found to be less in the case of latex. This is indicated in Table I by a comparison of pH values obtained for latices of various types by means of the antimony electrode and glass electrode, respectively, both of which were carefully calibrated with standardized buffer solutions. All the samples listed were diluted to 30 per cent total solids before measurement, except where indicated.

Inspection of Table I indicates that the difference in pH values between the two electrodes becomes less as the latex is purified to a greater degree—for example, the greatest difference is in normal latex, and the least difference is in the case of three-times-creamed latex. It is well known that hydroxy acids such as citric and tartaric acids, as well as certain sugarlike substances, affect the potential of the antimony electrode. It appears probable that some serum constituent of one of these types is responsible for the difference in results.

These data show that the pH values obtained with the antimony electrode are from 0.1 to 0.5 unit higher than those obtained with the glass electrode. While these differences are reasonably constant for the normal latices tested, this does not necessarily indicate that measurements with the antimony electrode can be accurately corrected to obtain the true pH. It seems entirely possible that samples of latex obtained from different plantations might require corrections of different magnitudes because of differences in the kinds and concentrations of serum constituents. Of course, the antimony electrode cannot be used in latex compounded with sulfur, sulfur-containing accelerators, and certain other chemicals. The use of the antimony electrode is not recommended for latex work.

The glass electrode when properly used is believed to be the most reliable and accurate means for measuring the pH of latex. Very constant and reproducible potentials are obtained, and there is no evidence that the glass electrode is poisoned or affected by any of the latex constituents or common compounding ingredients, with the exception of sodium hydroxide and sodium salts. However, the glass electrode is an empirical electrode and the values obtained by it in latex cannot be checked by a basic standard electrode such as the hydrogen electrode.

Full descriptions of the construction of the electrode and the potentiometric setups are given in manufacturers' pamphlets and in the literature (*7*).

Briefly, the complete cell is as follows:

Standard half-cell (calomel or quinhydrone)	0.120 *N* HCl (pH = 1.0)	glass	solution or latex pH = X	standard half-cell

That portion of the entire potential which measures the pH is, of course, the one arising at the glass-solution interface.

There are certain experimental precautions which have been found advisable on the basis of considerable experience in control work. While the commercially available glass shells are made with remarkable reproducibility, the calibration charts furnished with the glass electrode or printed on the dials of potentiometers of various types are not sufficiently accurate for all electrodes, particularly after the electrodes have been used in alkaline solutions for a considerable length of time. It is advisable to calibrate the electrodes daily in buffer solutions which have been standardized with the hydrogen electrode. The following buffer solutions have been found to be particularly practical for this purpose and if properly stored in stoppered Pyrex containers, they will remain at a constant pH for a period of 2 or 3 months.

Solution I:	
1.0 *N* KOH	50 cc.
2.0 *N* acetic acid	50 cc.
Distilled water to make (pH about 4.5)	500 cc.
Solution II:	
Anhydrous $KHCO_3$	10 grams
1.0 *N* KOH	50 cc.
Distilled water to make (pH about 10.0)	500 cc.

From the calibration data is obtained a calibration chart (pH versus e. m. f.) by drawing a straight line through the two experimental points. More careful calibrations have indicated that this procedure is justified.

On account of the high resistance of the glass electrode, it is necessary to use a very sensitive galvanometer. The Leeds & Northrup type 2500B is generally satisfactory for use with their glass-electrode shells, although difficulties are encountered if the galvanometer cannot be insulated from vibration. A vacuum-tube galvanometer which is marketed by the Hellige Company has been used successfully in control work. The Beckmann acidimeter, which is a portable vacuum-tube potentiometer, has been used successfully in one of the divisions of the company.

On account of the high resistance of the glass electrode, leakage of current around the electrode is occasionally encountered during humid weather unless proper precautions are taken. Such leakages are characterized by difficulty in balancing the circuit and by erratic behavior of the galvanometer. These difficulties can be eliminated by shielding the glass-electrode apparatus, and by making the leads to the galvanometer as short as possible. A suitable setup of this kind is illustrated in Figure 1. The glass electrode and calomel half-cell are enclosed in a metal box with a screen door, and water from a thermostat is pumped through the bottom of the container.

It cannot be too strongly emphasized that the potential of the glass electrode is affected by certain metallic ions above pH 9 to 10, one of the most important of which is sodium ion. This is illustrated by the graph taken from Dole (*1*) which shows the variation in salt error of the glass electrode with pH in solutions containing different metallic ions. In alkaline solutions above pH 10, the potential of the glass electrode is depressed by sodium ion and to a lesser extent by potassium ion. This means that pH measurements of alkaline latices containing sodium hydroxide or sodium soaps would be considerably in error.

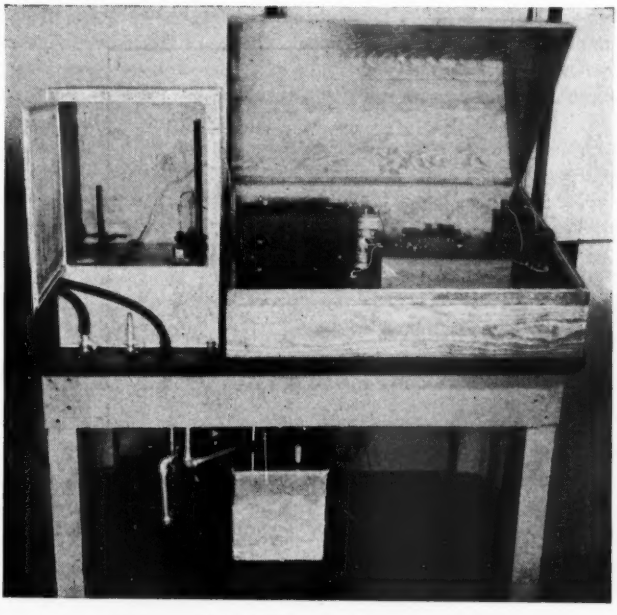

FIGURE 1. pH APPARATUS AND THERMOSTAT

Surface Tension

The surface tension of latex is often assumed to be an indication of the foaming and related properties of latex. This relationship has not been too clearly established, but inasmuch as considerable importance is often attached to surface tension values, a standard and accurate procedure should be used for measuring them. Of the methods available, the capillary-rise and bubble-pressure methods are unsuitable. Accurate results can be obtained by the drop-weight method, but the technic is somewhat more cumbersome than is desirable for control.

The ring method is simple in manipulation and gives

accurate values if the results are calculated properly. However, very inaccurate results are often obtained because no attention is paid to the important corrections required for the experimental data. Inasmuch as the theory and experimental technic have been treated by Freud and Freud (*2*), and by Harkins and Jordan (*4*), only the more common sources of experimental error will be discussed in this paper.

In outline, the ring method consists in determining the maximum pull of the liquid on a circular wire ring when the ring is withdrawn, and from this pull the surface tension can be calculated. A number of types of apparatus have been

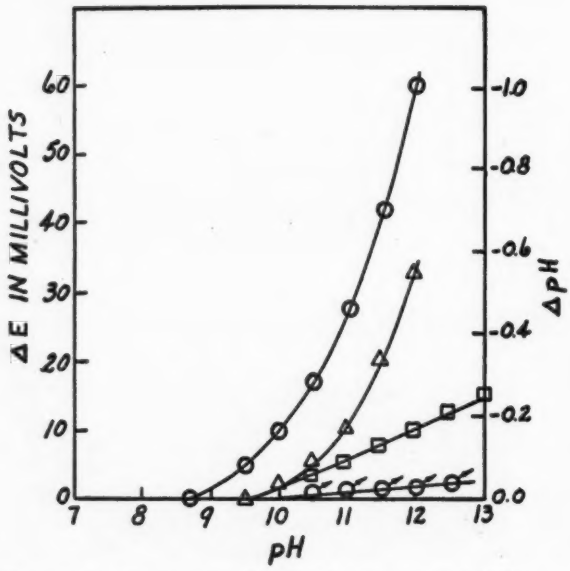

FIGURE 2. ERRORS OF GLASS ELECTRODE IN 1 *N* SOLUTIONS (AFTER DOLE)

△ Li^+, ○ Na^+, □ K^+, ♂ Ba^{++}

developed, all of which consist in principle of a torsion, spring, or chainomatic balance. Directions for operation are given in manufacturers' pamphlets, but the following experimental points should be stressed:

Great care should be taken to maintain scrupulous cleanliness. Glassware should be cleaned with chromic acid solution, and the ring, after cleaning in chromic acid, should be heated to red heat in the oxidizing portion of a Bunsen flame. In this connection care should be exercised to make sure that any salts or latex have been removed from the ring before flaming, or serious damage will result. The wire of the ring should all lie in one plane and the ring should hang in

such a way that its plane is parallel to the surface of the liquid.

One of the most common sources of experimental error is that the liquid is often contained in too small a dish, or in a watch glass, with its surface open to evaporation in the air. Accurate measurements can be obtained under such conditions only by accident. It is preferable that the liquid be contained in a fairly large dish which is enclosed in a deep vessel, as illustrated in Figure 3. The outer vessel is covered with a plate with a hole in its center of sufficient size to permit connection of the ring to the balance arm with a fine platinum wire. This is particularly important in the case of latex because of the tendency of this material to "skin over" on its surface. Such skinning over, although invisible to the eye, may increase the values obtained by several dynes. In order to ensure a fresh surface, it is advisable to overflow the inner dish before making measurements.

Another common source of error lies in the assumption that either the scale gives values directly in dynes per cm. or, in the case of certain apparatus, that the reading in grams is correct. It is important that the balance be directly calibrated in grams, and that the surface tension be calculated from the total pull on the ring by the method given below.

Many surface tension results obtained by the ring method which have appeared in the literature are of no value because it has been incorrectly assumed that the surface tension is related to the pull on the ring by the equation

$$\gamma = \frac{Pg}{4\pi R}$$

where P is the total pull in grams on the ring, g is the acceleration of gravity, and R is the radius of the ring. In order to obtain correct surface tension values, the right-hand member of the above equation must be multiplied by a correction factor to give the equation

$$\gamma = \frac{Pg}{4\pi R} F$$

where the correction factor, F, is a function of $\frac{R^3}{V}$ and $\frac{R}{r}$. V is the volume of liquid raised by the ring above the free surface and is equal to the total pull in grams divided by the density. $\frac{R^3}{V}$ is therefore equal to $\frac{R^3 d}{P}$. $\frac{R}{r}$ is the ratio of the radius of the ring to the radius of the wire from which it is made, and its value is generally given by the manufacturer. Tables of correction factors for various values of $\frac{R^3}{V}$ and $\frac{R}{r}$ are given by Harkins and Jordan (*4*). From these tables a correction curve for any particular ring (whose $\frac{R}{r}$ value is of

course constant) can be constructed. Unless such corrections are made, the results may be considerably in error, depending upon the dimensions of the ring and the material measured.

This is illustrated by the following comparison of corrected and uncorrected ring method results with results obtained by the drop-weight method (Table II). The latices were diluted as indicated in the second column.

In the case of the ring used in these experiments, the uncorrected results obtained by the ring method are approximately 3 dynes per cm. higher than the correct values.

Considerable difficulty has been found in obtaining

FIGURE 3. SURFACE TENSION APPARATUS

reproducible results on latex if the total solids content is substantially above 40 per cent, because the viscosity is sufficiently great to prevent the liquid from attaining its equilibrium shape in a reasonable length of time. For this reason, it is desirable to make surface tension measurements on concentrated latex at a standard condition—as, for example, 40 per cent total solids and 0.5 per cent ammonia.

Viscosity

The flow properties of latex and latex compounds are frequently of importance in the handling and processing of these materials. As illustrations may be cited dipping and spreading processes. For practical reasons it is convenient to treat the flow properties of latex in a special way, introduc-

ing some new terminology. It will be found that viscosity data can be expressed in this terminology in a form which is convenient in the making of practical calculations.

TABLE II. COMPARATIVE RESULTS

	Total Solids	Scale Reading	Total Pull (P)	Surface Tension Ring method[a] Uncorrected	Ring method[a] Corrected	Drop-weight method
	%		*Gram*	*Dynes per cm.*		
Normal latex, A	30	38.7	0.316	38.7	35.6	35.9
Concentrated latex, A	40	34.9	0.285	34.9	31.9	32.2
Concentrated latex, B	40	39.0	0.318	38.9	35.9	35.7
Benzene	—	30.7	0.251	30.8	28.0	28.2[b]

[a] R = 0.637 cm., R/r = 38.8.
[b] Value taken from International Critical Tables.

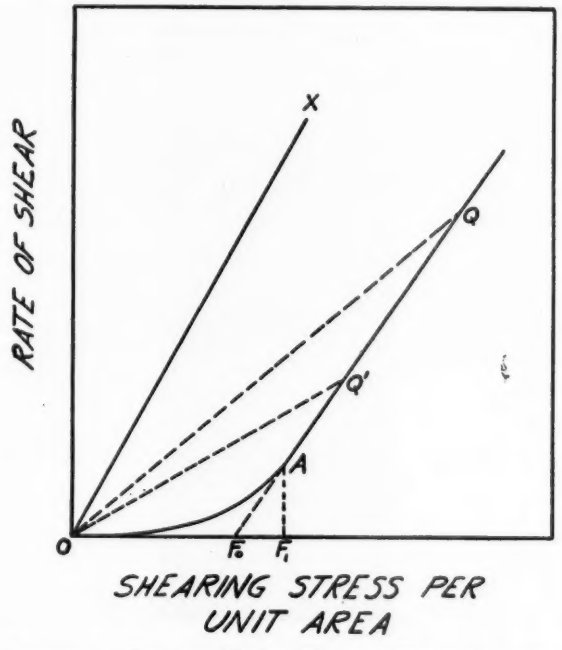

FIGURE 4. SHEARING STRESS–RATE OF SHEAR DIAGRAM
For a Newtonian liquid (OX) and for a Non-Newtonian liquid like latex ($OAQ'Q$)

THEORETICAL. A Newtonian or perfectly viscous liquid is characterized by the existence of a linear relationship between an impressed shearing stress and the rate of shear produced. The coefficient of viscosity of such a liquid is defined as

$$\eta = \text{coefficient of viscosity} = \frac{\text{shearing stress per unit area}}{\text{rate of shear produced}} \quad (1)$$

and is a constant over the range of shearing stresses in which the liquid does not exhibit turbulence. The situation is pictured by the solid straight line OX in Figure 4, and the coefficient of viscosity is equal to the reciprocal slope of the line OX.

Liquids in which the relationship between shearing stress and rate of shear is not linear are termed non-Newtonian. Latex is such a non-Newtonian liquid, and a typical stress-rate of strain diagram is shown by the solid line in Figure 4.

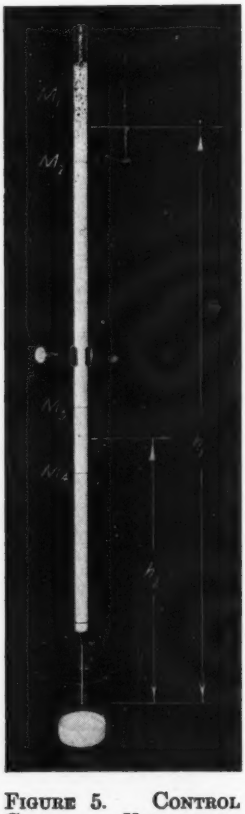

FIGURE 5. CONTROL CAPILLARY VISCOMETER

Now the definition of the coefficient of viscosity remains unchanged in the transition from Newtonian to non-Newtonian liquids and is defined by Equation 1. It is thus plain that the value of η for a non-Newtonian liquid is not a constant over the range in which no turbulence occurs. For instance, η at Q in Figure 4 is the reciprocal slope of OQ, whereas η at Q' is the reciprocal slope of OQ'. Consequently in the case of a non-Newtonian liquid it is impossible to use the coefficient

of viscosity at one shearing stress to calculate the rate of shear at another shearing stress.

It is an experimental fact that the stress-rate of strain diagram of latex becomes a straight line for a range of shearing stresses above a given value. This situation is represented by the portion of the solid curve to the right of A in Figure 4. As the shearing stress increases, the coefficient of viscosity of the non-Newtonian liquid approaches the reciprocal slope of the straight portion of the curve. These considerations suggest the following definition in connection with non-Newtonian liquids:

η' = limiting coefficient of viscosity
= reciprocal slope of straight portion of stress–rate of strain curve

In the case of a Newtonian liquid the quantity η determined at a single shearing stress completely specifies the flow properties of the liquid throughout the shearing stress interval in which no turbulence occurs, since the straight line constituting the stress-rate of strain curve passes through the origin of the stress-rate of strain diagram. This is not true in the non-Newtonian case, and in order to complete the specification of flow properties in the straight portion of the curve, it is necessary to know the stress intercept of this straight portion, produced. This stress intercept is denoted by F_0 in Figure 4 and is called the yield point.

The quantities η' and F_0—i. e., limiting coefficient of viscosity and yield point—are constants for any given latex, and from them may be calculated the flow properties of the latex at any point on the straight portion of the stress–rate of strain curve by means of the equation

$$g(F - F_0) = \eta' S \qquad (2)$$

where F = absolute shearing stress per unit area in grams per sq. cm.
F_0 = yield point
g = acceleration of gravity
S = absolute rate of shear

This method has the advantage over the use of true viscosity that only two quantities, η' and F, must be dealt with instead of a series of values, η.

This treatment ignores the nonlinear portion of the stress–rate of strain curve in Figure 4, but it should be clearly realized that the introduction of this treatment was intended solely to simplify calculations of flow properties of latex in the linear portion of the stress–rate of strain curve. Many practical problems fall within this classification. In cases in which the nonlinear portion of the stress–rate of strain curve must be dealt with, it is probably best to resort to the use of true viscosity.

METHODS. In the experience of the authors, two methods

of measuring viscosity have been used and found satisfactory for control work: the capillary-flow method and the rotating-cylinder method. Both provide rapid and precise means of measuring the flow properties of latex. The former possesses the advantage that the apparatus may be made from materials stocked in the laboratory. For the control of raw latex the capillary-flow method employing the simple apparatus shown in Figure 5 fulfills all requirements, but with many compounds either a modified capillary-flow apparatus (Figure 6) or a rotating-cylinder viscometer (Figure 7) must be resorted to.

The rotating-cylinder apparatus possesses a wider field of applicability than the capillary-flow setup, but the details

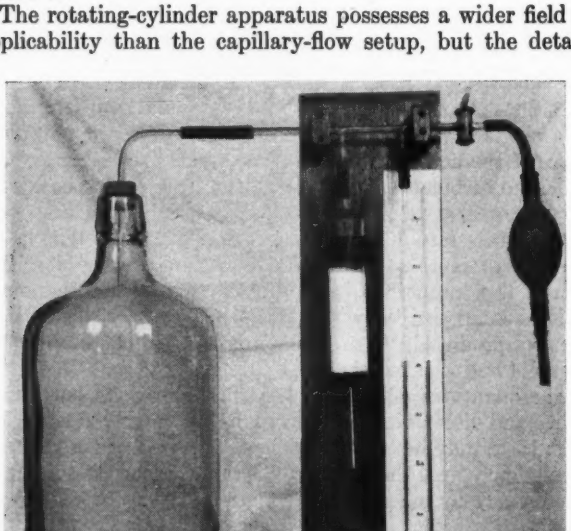

FIGURE 6. MODIFIED CAPILLARY-FLOW APPARATUS

of its construction make it rather expensive. The rotating-cylinder method can be made to replace the capillary method in all departments of latex work with the exception of normal latex, which has such a low viscosity as to be out of the most useful range of the rotating-cylinder apparatus with dimensions specified by Mooney and Ewart (*8*). Data on viscosity and limiting viscosity as obtained by these two methods are found to be in good agreement if the points obtained on the stress-rate of strain diagram are on the straight portion of the curve. Yield point results show variations, particularly in compounds of high viscosity. There are reasons for feeling that the rotating-cylinder values are more reliable. These difficulties are probably traceable to

the fact that latex does not possess an actual yield point. It is easily shown that the yield value as calculated on the basis of preceding definitions is actually to some extent dependent on the nature of the nonlinear portion of the real stress–rate of strain diagram.

Recent work on the falling-sphere method has resulted in apparatus which may very likely be suitable for use in latex. The writers have had no experience with this method. In general the capillary-flow and falling-sphere methods possess a disadvantage when compared to the rotating-cylinder method—namely, that they are dynamic rather than kinematic methods, and require a knowledge of the density of the material under test.

In order to render the results of viscosity measurements comparable, it is necessary to carry out all determinations on a given type of latex at the same total solids content. A precaution which should be observed in preparing the latex for measurement is to eliminate all gas bubbles. This may be done by deaerating the latex under reduced pressure for several hours.

Capillary-Flow Method. In the capillary-flow method of measuring viscosity the shearing stress is usually produced by the hydrostatic pressure of the liquid above the capillary tube. The apparatus is pictured in Figure 5. It consists of an 80-cm. glass tube 1 cm. in inside diameter with scratches M_1, M_2, M_3, M_4 as shown and a capillary tube of known dimensions inserted in the lower end of the 80-cm. tube by means of a rubber stopper. The method consists of measuring the lengths of time necessary for two equal given volumes of latex, as estimated by the passage of the meniscus through two intervals bounded by scratches on the 80-cm. tube, to flow through the capillary under two different hydrostatic pressures. In terms of Figure 5 the following dimensions have been found suitable for the manipulation of latex:

h_1 and h_2 = heights of midpoints of intervals M_1M_2 and M_3M_4, respectively, above bottom of capillary (h_1 = 65 cm.; h_2 = 30 cm.)
R = radius of capillary (R = 0.040 ± 0.002 cm. for normal latex; R = 0.070 ± 0.004 cm. for creamed or centrifuged latex)
L = length of capillary (10 cm.)
V = volume included in each of intervals M_1M_2 and M_3M_4 (10 cc.)

The numerical values of h_1, h_2, R, and L are so chosen that the two stresses under which the rates of flow are measured both fall on the linear portion of the stress–rate of strain diagram.

With the aid of the following additional notation it is possible to write down formulas for viscosity and yield point in terms of the above characteristics of the apparatus:

t_1 and t_2 = times in seconds for latex meniscus to pass through intervals M_1M_2 and M_3M_4, respectively
d = density of latex in grams per cc.
g = acceleration of gravity (980.6 grams per second per second)
T = temperature in ° C.
η = coefficient of viscosity in poises at temperature T
η_{25} = coefficient of viscosity in poises at 25° C.
η' = limiting coefficient of viscosity in poises at temperature T
η'_{25} = limiting coefficient of viscosity in poises at 25° C.
F_0 = yield point in grams per sq. cm. at T° C.
V = volume of latex (= weight of latex/density of latex)

Then

$$\eta' = K_1 \frac{t_2 t_1}{t_2 - t_1}$$

$$F_0 = K_2 - K_3 \frac{\eta'}{t_2}$$

where

$$K_1 = \frac{\pi R^4 g d\ (h_1 - h_2)}{8\ LV}$$

$$K_2 = \frac{3Rh_2 d}{8L}$$

$$K_3 = \frac{3V}{\pi R^3 g}$$

In the testing of highly viscous samples a modified capillary-flow apparatus is sometimes desirable. The modification consists of augmenting the hydrostatic pressure used in the simple apparatus by means of an external superimposed pneumatic pressure. The apparatus for this procedure is pictured in Figure 6. The pneumatic pressure is developed with the aid of a syringe bulb by pumping air into the large glass bottle reservoir shown in the figure. When the desired pressure, as read on the U-tube differential manometer, has been attained, the stopcock in the line leading to the syringe bulb is closed and latex is allowed to flow through the capillary for a given length of time into a large weighing dish. The latex is weighed to an accuracy of 1 per cent, and the process is repeated at one or more different values of the impressed pneumatic pressure. It will be noted that the 80-cm. tube of the simple apparatus has been replaced by a short tube of much larger diameter. The following additional notation will be necessary in order to write down formulas:

d_1 = density of latex in grams per cc.
d_{Hg} = density of mercury in grams per cc.
P_1 and P_2 = pneumatic pressure in cm. of mercury
h_1 and h_2 = average heights in cm. of top of latex column above bottom of capillary at pressures P_1 and P_2, respectively
w_1 and w_2 = weights in grams of liquid delivered at pneumatic pressures P_1 and P_2, respectively, in times t_1 and t_2, respectively

$$\eta' = K_4 \frac{d_{H_2}(w_2P_1 - w_1P_2) + d_1(w_2h_1 - w_1h_2)}{w_1w_2} \frac{t_1t_2}{t_2 - t_1} d_1$$

$$F_0 = K_5P_2 - K_6 \frac{\eta' w_2}{d_1t_2}$$

where

$$K_4 = \frac{\pi R^4 g}{8L}$$

$$K_5 = \frac{3R}{8L}$$

$$K_6 = \frac{3}{\pi R^3 g}$$

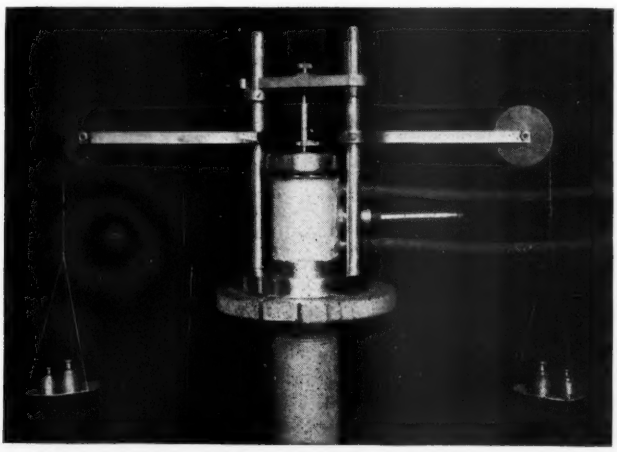

FIGURE 7. ROTATING-CYLINDER VISCOMETER

ROTATING-CYLINDER METHOD. In this case the shearing stress is produced by falling weights which, by means of a system of strings and pulleys, cause rotation of the cylinder. The complete theoretical expression for the instrument constant may be found in the afore-mentioned article by Mooney and Ewart, but it is too complex to be reproduced here. The form of the equation from which the viscosity of a Newtonian liquid may be calculated from rotating-cylinder viscometer data is, using the same notation as in the discussion of the capillary flow method with some additions

$$\eta = KMt \qquad (3)$$

where K = instrument constant, experimentally determined (with standard liquid)
M = total mass of weights and pans
t = time in seconds for one revolution of rotor

The procedure in going to non-Newtonian liquids is very similar to that employed in discussing the capillary flow

method. Instead of two pressure heads, two values of M are employed.

Then
$$\eta' = K(M_1 - M_2)\frac{t_2 t_1}{t_2 - t_1} \tag{4}$$

The value of M corresponding to the yield point F_0 is

$$M_0 = M_2 - \frac{\eta'}{Kt_2} = \frac{M_2 t_2 - M_1 t_1}{t_2 - t_1}$$

$$F_0 = LM_0 \tag{5}$$

where

$$L = \frac{3C}{4\pi^2 R_0^2 l_0 \left[1 + \frac{R_0}{3l_0 \sin \Theta_0}\right]} \tag{6}$$

C = circumference of pulleys
R_0 = mean radius of inner and outer cylinders as defined by

$$\frac{1}{R_0^2} = \frac{1}{2}\left[\frac{1}{R_1^2} + \frac{1}{R_2^2}\right]$$

R_1 and R_2 being the radii of the rotor and stator, respectively
Θ_0 = mean angle between bottom of stator and bottom of rotor
l_0 = effective length of cylindrical section of rotor

Temperature Correction. The capillary methods as described above have the disadvantage that thermostatic temperature control is difficult. However, if measurements are made within a few degrees of 25° C., it has been found satisfactory to correct the viscosity values for temperature by means of the following equations:

$$\eta_{25} = \eta\ [1 + 0.02\ (25 - T)] \tag{7}$$

$$\eta'_{25} = \eta'\ [1 + 0.02\ (25 - T)] \tag{8}$$

These equations are of a form which is known to be valid over small temperature intervals for water. The data of the following table permit the calculation of an average temperature coefficient for viscosity measurements in latex of 2.2 per cent per degree Centigrade, but the accuracy of the data is not sufficient to warrant considering the difference between 2 and 2.2 per cent as significant. In short, Equations 7 and 8 represent the best available method of temperature correction of viscosity data. Over a 5° interval on each side of 25° C. they are sufficiently accurate for practical purposes, except in the case of latices of very high total solids content or those highly thickened with soaps, gums, etc.

Temperature, °C.	At Total Solids: 44%	46%	48%	50%
25.0	8.50	10.0	11.4	14.2
30.6	7.78	9.62	10.4	12.3
36.1	6.24	7.91	9.24	10.0

RELATION BETWEEN η AND η'. As a matter of interest the following relation between the true and limiting coefficients of viscosity is listed:

$$\eta = \eta' \frac{F}{F - F_0} \tag{9}$$

where F is the absolute shearing stress

Mechanical Stability

In the course of handling and processing, latex is often subjected to violent shearing stresses produced by mechanical treatments such as pumping and stirring, which tend to destabilize it. When it is considered that such situations as these

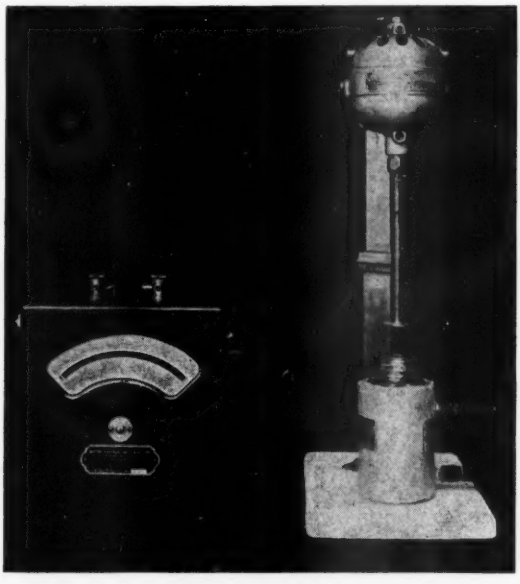

FIGURE 8. APPARATUS FOR MECHANICAL STABILITY TEST

are rather frequently encountered, it is unfortunate that there is no adequate means of evaluating the ability of all types of latex to withstand the effects of mechanical agitation. A major hindrance to the setting up of a general mechanical stability test lies in the lack of any precise concept of stability. The notion is a rather vague one at best and varies considerably in different connections.

In the experience of the authors, the high-speed stirring test is the only one which gives results even approximately in accord with the practical stability behavior of latex. The test, apparatus for which is shown in Figure 8, consists of stirring a sample of latex until it coagulates. The stirring

is done by means of a small slotted propeller blade which is driven by a high-speed Hamilton Beach motor. It fails in two cases: (1) in very thick compounds, (2) in compounds containing foaming agents. In the first case, the propeller blade tends to beat out a cavity in the latex so that actual stirring ceases after a short time. In the second case, the entire sample may be whipped to a very stable foam which will not coagulate. In uncompounded normal, creamed, and centrifuged latex and in many latex compounds, however, the high-speed stirring test for mechanical stability possesses the most practical advantages of any test known to the authors at present.

The customary procedure for measuring mechanical

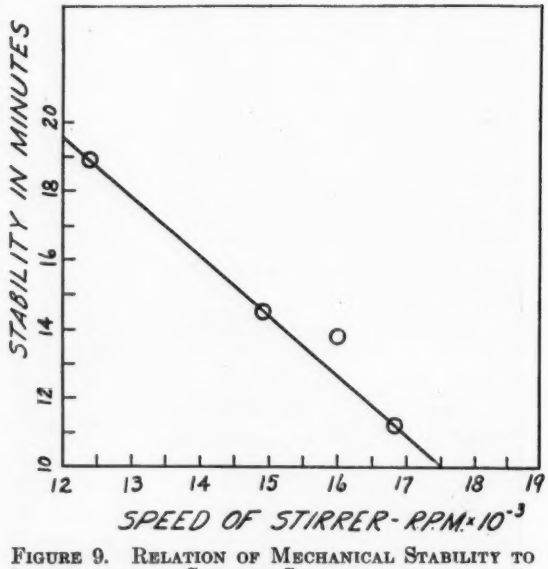

FIGURE 9. RELATION OF MECHANICAL STABILITY TO SPEED OF STIRRER

stability has been modified in two important details. These are (1) the application of a correction for the speed of the motor, and (2) the method of selecting the end point. Another item of importance is temperature control.

The speed at which the latex is stirred has been found to produce an inverse linear variation of the time required for coagulation. The data to support this conclusion, presented here, were obtained on one normal latex at 26.4 per cent total solids at various motor speeds.

Speed of Motor *R. p. m.*	Stability *Min.*
12,400	18.9
14,900	14.3
16,000	13.8
16,840	11.2

From the data a table of correction factors to 15,000 r. p. m.. the arbitrarily chosen standard speed, can be constructed (Table III).

TABLE III. CORRECTION FACTORS

Speed of Motor *R. p. m.*	Correction Factor
12,000	0.74
12,500	0.77
13,000	0.80
13,500	0.85
14,000	0.90
14,500	0.94
15,000	1.00
15,500	1.07
16,000	1.14
16,500	1.22
17,000	1.32

When a mechanical stability value is obtained at a motor speed different from 15,000 r. p. m., multiplication of the observed value by the appropriate correction factor from Table III will give the value which would have been obtained at 15,000 r. p. m. For example, if a stability of 10 minutes were obtained at a motor speed of 13,500 r. p. m., then the corrected stability would be given by $10 \times 0.85 = 8.5$ minutes. The motor speed should be measured with a tachometer at a standard time, say 30 seconds, after the beginning of a determination.

In the case of the end-point selection in this determination, personal errors have been eliminated by the following means:

A milliammeter is connected in series with the motor, and current consumption is plotted against time from the beginning of the determination. When coagulation sets in, the general tendency of the current consumption will be to increase as the load on the motor is increased by adherence of coagulum to the propeller blade. During the first stages of coagulation, there are frequent large jumps in the current consumption, occasioned by pieces of coagulum which adhere to the blade and are then thrown off, thus causing short periods of alternate labor and racing on the part of the motor. Readings should be continued until there is a steady and rapid rise in current consumption with time, an occurrence caused by complete coagulation of the sample. The time at which this rise starts is taken as the end point.

For purposes of temperature control of the sample under test, the base of the stand on which the motor is mounted should be provided with a water jacket through which water at a standard temperature, say 25° C., can be circulated. This control is of considerable importance, since a difference of 10° in temperature may make a large difference in the stability value obtained.

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Determination of Free Carbon in Rubber Goods

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THIS paper is presented with the aim of rendering more accurate and simple the difficult analytical determination of carbon black in rubber.

A survey of the methods proposed for this determination reveals that they are not as short, easy, or accurate as might be desired. Smith and Epstein (*5*) have discussed what is probably the most widely used method, nitric acid decomposition of the rubber sample. In its essentials, this is the method recommended to the AMERICAN CHEMICAL SOCIETY in 1922 by the Committee on Methods of Analysis of the Rubber Division (*1*), and was recommended (*6*) to German chemists with the variation of making the filtration through hardened filter paper. Another variation, recommended by the Research Association of British Rubber Manufacturers (*2*), calls for filtration through a thick layer of kieselguhr, using carbon tetrachloride in the nitric acid. In addition, two unique methods have been recommended (*4*), which call, respectively, for decomposition of the sample in hot molten paraffin with subsequent centrifuging of benzene and ether solutions and for distillation of the rubber in an atmosphere of nitrogen. The consensus of opinion seems to be that the nitric acid decomposition is the simplest method and accurate enough for technical purposes. This paper will be confined to improvements upon this method.

Procedure

Weigh samples of such size that the amount of carbon black does not greatly exceed 75 mg. and place in a 250-cc. beaker. Add 10 to 15 cc. of concentrated nitric acid and allow to stand at approximately 60° C. until the rubber is disintegrated. Add 50 cc. more of concentrated nitric acid, taking care to wash down the sides of the beaker, and heat on the steam bath for 1 hour. Filter before it is cool with moderate suction through ignited Gooch crucibles having a medium layer of asbestos, and wash well with hot concentrated nitric acid. It is essential that all the black be rinsed from the beaker at this stage. Turn off the suction when the carbon in the crucible is still covered with a small amount of the last nitric acid wash.

Empty the filter flask (this is important), pour into the crucible a hot mixture of equal parts of acetic acid, acetone, and chloroform, and continue the filtration. Wash the black with a warm 50–50 mixture of acetone and chloroform until the filtrate is colorless. Wash with hot 10 per cent sodium hydroxide until three washings have come through colorless. Wash three times

with 15 per cent by volume of hot hydrochloric acid and once with 5 per cent by volume of warm hydrochloric acid. Remove the crucibles and clean the outside with a cloth moistened with the acetone-chloroform mixture. Dry in the 110° C. oven for 2 hours. Cool in a desiccator and weigh rapidly. Burn off the carbon and reweigh. The difference in weight, corrected for clay if present, represents approximately 105 per cent of the carbon black originally present. To obtain the correction factor for clay, multiply the amount of clay present in the sample by 14 per cent, or multiply the sum of SiO_2 and R_2O_3 weights in the sample by 16.3 per cent, and subtract this figure from the total ignition loss.

It seems to be important that the carbon black should not dry during filtration. Drying in the nitric acid wash seems to pack the layer of carbon and thus slow the filtration. Small particles of black will not be retained on the filter if the nitric acid is completely filtered through before the addition of the acetone–acetic acid–chloroform mixture. Drying of the black during the later washings seems to have no effect beyond reducing the effectiveness of the wash solutions.

Discussion

It has been the authors' experience that when more than 75 mg. of carbon black are to be filtered from a nitrated rubber solution, the filtration usually becomes extremely slow. Rubber goods, as, for instance, tread stocks (*3*), now contain increased amounts of carbon black as compared with those used when the nitric acid method was first devised. Therefore, in the analysis of stocks containing over 15 per cent black, the authors recommend the use of a sample smaller than the 0.5 gram originally specified. For rapid determinations on tread stocks containing in the neighborhood of 30 per cent black, the sample size should not exceed 0.25 gram.

The standard practice of extracting samples with acetone and chloroform is unnecessary. This is shown by analyses of the same tread stock extracted and not extracted:

	Carbon Black %		Carbon Black %
Extracted sample	31.28	Unextracted sample	31.28
	31.12		31.32
	31.72		31.28

In the change of wash solutions from hot nitric acid to acetone and chloroform, small particles of black are frequently lost, acetone having a more detrimental effect than the mixture of acetone and chloroform. Whether this difficulty is encountered because of the wetting tendency of acetone or because of the charge upon the particles is not known. The authors' experiments have shown that an intermediate wash of equal parts of acetone, chloroform, and acetic acid has less tendency to disperse the black than immediate washing with either acetone or acetone and chloroform, as recommended in prior methods.

A common type of rubber stock for mechanical goods is a carbon black–clay mix. Clays have an ignition loss and give too high a value to the carbon black determination of such a stock. The Committee on Methods of Analysis of the Rubber Division of the AMERICAN CHEMICAL SOCIETY has recommended (*1*) treating the clay residue with sodium hydroxide. The authors have found that such treatment is futile. An analysis of an average clay showed that 85 per cent was insoluble in alkali, and the component showing ignition loss was the insoluble portion. Since they know of no way to remove this insoluble clay prior to the ignition, it is fortunate that the ignition loss for practically all silicates used in the rubber industry is in the neighborhood of 14 per cent, and a correction factor can therefore be applied. Knowing the amount of clay in the sample, we can subtract 14 per cent of this value from the ignition loss. If the original clay content is not known, we can subtract from the ignition loss 16.3 per cent of the sum of SiO_2 and R_2O_3 weights in the sample. The authors recommend this method of correction as fairly accurate. The correction so applied may amount to 2 or 3 per cent. Slight differences in composition of clays will affect the correction factor only to a small degree.

Washing the black with sodium hydroxide is still necessary, however, to remove part of the mineral rubber not removed by nitric acid or acetone and chloroform, as well as other material adsorbed from the nitric acid solution of the rubber sample. Analyses were made of the following stocks by the method here recommended; analyses were also made by the same method, omitting only the sodium hydroxide and subsequent washes.

	Without NaOH Wash	With NaOH Wash		Without NaOH Wash	With NaOH Wash
	%	%		%	%
30% black	31.16	30.84	30% black	33.28	30.72
	31.04	30.48	10% mineral rubber	33.68	30.24

The reaction product of nitric acid upon carbon black is probably some stable form of graphitic acid (*5*). It cannot be reduced by formaldehyde. Smith and Epstein have stated (*5*) that carbon black is recovered from nitric acid in an amount approaching 105 per cent of the original weight. The authors have found that unless washed with water or sodium hydroxide, the reaction product will have approximately a 2 per cent higher weight. They do not, however, recommend washing with water, since sodium hydroxide serves the same purpose and does not have water's tendency to cause loss of the black in filtration. The water-soluble portion of this oxidation product is believed to be gases adsorbed from the nitric acid. These must be washed out.

The authors have found in a large number of determinations of carbon black in rubber by the nitric acid decomposition method that the results were slightly higher than the

theoretical 105 per cent, and that carbon black does not gain weight when treated with hydrochloric or acetic acids and then dried. The higher results are therefore not due to adsorbed hydrochloric or acetic acids, but may be attributed to the difficulty of freeing the carbon particles from adsorbed material contained in the average rubber mix.

It has been the authors' experience that the results vary but little whether the nitric acid solution of rubber is filtered immediately or allowed to cool. Allowing the black to settle apparently does not hasten the filtration; therefore, filtration is recommended while the solution is at least warm.

Although lead is rarely used today in the compounding of rubber, it must be removed if present (*1*). A negligible error is caused by the presence of barium and calcium sulfates.

Summary

The carbon black analysis should not be made without a consideration of the nature of the original stock. The size of the sample must be related to the black content. To lessen time consumed in this analysis, preliminary extraction of the sample should be omitted. The correction factor for clay must be applied. By the revised method greater accuracy is obtained, although there is still a tendency for the results to be higher than calculated. Precision in this method seems to depend mainly upon accuracy of weighing and avoiding the loss of small particles of black.

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The Preparation of Thin Films

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VARIOUS means which have been suggested for the preparation of thin films of rubber and similar materials include their deposition on glass, porcelain, sheet metal, and mercury. The use of rigid surfaces is open to the objection that in the case of some materials the adhesion of the film may be troublesome. The removal from such surfaces, of films of materials which are subject to permanent deformation on stretching, tends to lessen the uniformity of their thickness. In connection with the study of the permeability to gases of thin films unsupported by fabric, a satisfactory and simple method was found for their preparation.

Regenerated cellulose sheeting, extensively employed for wrapping purposes, is used as the base upon which the films are deposited. For this purpose it is essential to employ sheeting which has not been coated with a moisture-proofing composition. The material is held taut between closely fitting steel hoops. The film-forming materials are applied in the form of their solutions in volatile solvents. Uniformity of film thickness is obtained by using dilute solutions and a plurality of coats. After the solvents have evaporated and, when necessary, the deposited film has been cured at elevated temperatures, the uncoated surface of the regenerated cellulose is covered with water. Within a short time the film may be readily loosened and removed without any appreciable stretching or other damage.

This method of preparation is obviously suitable only for films of materials not appreciably affected by moisture. Thin films of rubber, Thiokol, Neoprene, cellulose derivatives, and oleoresinous varnishes were successfully prepared in this manner. The length of time that the film is in contact with the moist regenerated cellulose is not sufficient, with these materials, to produce any change in their appearance.